FOLLES AND FORGERIES: an appraisal of the composition of Roman copper-alloy coinage of the mid-third to mid-fourth centuries A.D. from Britain.

Thesis submitted for the degree of Doctor of Philosophy.

1994

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ABSTRACT

This thesis deals with the effects of the burial environment on complex copper-alloy coins and how these can result in non-representative data leading to erroneous numismatic interpretations. Three main periods of Romano-British coin copying are investigated compositionally in order to demonstrate the value of a more rigorous methodology. Samples from selected hoards are used to examine the period of Radiate copying (AD 270's - 280's), the period of Constantinian copying (c. AD 341-346) and the period of the 'FEL.TEMP.' copies (c. AD 354-364). In addition to this well preserved hoard material, a small hoard of corroded together Constantinian nummi from Richborough was analysed in its entirety and is compared with numismatically identical hoard material, together with excavated site finds covering all three periods.

The problems of creating a suitable sampling strategy and the specific problems related to the sampling of ancient numismatic material are discussed. The topic of segregation in complex alloys is examined, followed by a discussion of corrosion theory. The analytical techniques employed in this study are atomic absorption spectroscopy and electron-probe microanalysis. The choice and limitations of these techniques are assessed for numismatic research.

Segregation and corrosion studies on four Radiates demonstrates that these are seldom adequately overcome using the accepted 'non-destructive' analytical techniques. A 3-D spatial study of corrosion is conducted using computerised imaging and database links on the Richborough hoard. This suggests that the bulk composition of individual coins can be altered by corrosion even within a single hoard if the differences in preservation are sufficiently pronounced.

The application of a well developed sampling strategies and appropriate analytical procedures can provide results of high precision for numismatic studies. Measured application of univariate and multivariate statistical methods are utilized in order to assess variations and similarities in the data sets. This approach has provided new information on the use of copper-alloys and the technology of coin production for both official Roman coins and their copies during this period.

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Acknowledgements

I have been very lucky in being able to call on the assistance and support of a number of people, without whose patience and understanding this project would not have been completed. I would first like to thank my tutors at Leicester University, in particular Prof. Graeme Barker and Graham Morgan, for providing the initial encouragement. This project was made possible by a grant from the Science and Engineering Research Council (SERC).

I would like to thank my supervisors. Dr. Richard Reece and Dr. John Merkel for their enthusiasm and guidance. In particular I wish to thank Richard Reece for his continual support of my work, from my undergraduate days, through the trauma of grant application, to the reading of drafts. I should also thank Richard Reece for his assistance in gaining permission to sample the various groups of material upon which this thesis is based. I also thank Dr. John Merkel for his guidance and particularly for his support in gaining and maintaining the hardware (and software) which produced the data presented here.

I also wish to thank: Dr. Clive Orton for invaluable help with the statistics used here, Dr. D.R. Griffiths and Kevin Reeves, our technician, for outstanding patience and valuable insights into many of the problems encountered and Dr. Mike Czwarno for coaching me into the world of computers and general advice. Thanks must also go to Mike Cowell and Dr. Jack Williams for technical advice. For permission and access to sample material I must thank Robert Zeepvat (Milton Keynes Archaeological Unit), Robin Holgate (Luton Museum), Fraser Hunter (National Museum of Scotland), Andrew Burnett (British Museum) and Adrian Tribe (English Heritage). I also owe considerable thanks to Ian Wetherhogg and his associates at QA Design Ltd, who assisted greatly with the rather unorthodox use to which I put Microstation.

I would also like to thank my colleagues, Alan Horsler, Peter Guest, Dr. Ziad al Ahmed, Craig Meredith and Sharada Srinivasan for valuable discussions. Stuart Laidlaw for photographic advice, Helen Marshal for her assistance in the Photogrametry department and Dr. Chris Salter for running the samples on the micro-probe at the Research Laboratory for Archaeology and the History of Art in Oxford.

Finally, but by no means least, I wish thank my parents for their support and Irit Narkiss for her patience and for reading numerous drafts.

Chapter 1:
The Introduction

"Archaeology is rather like a vast, fiendish jigsaw invented by the devil as an instrument of tantalising torment, since:

a) it will never be finished.

b) you don't know how many pieces are missing.

c) most of them are lost forever.

d) you can't cheat by looking at the picture." (Bahn 1989,5)

1.1 General Introduction.

A short while before I finished the bulk of the practical work on which this thesis is based I was asked to give a joint seminar with one of my two supervisors, Dr. Richard Reece. He told me that he wanted to run the seminar as a 'question and answer' type double-act, starting from the standpoint that as people have been analysing Roman coins for over 100 years, what had I been doing for the past two and a half and why? This struck me as a good starting point for this thesis. It is all too easy to become so involved with the scientific minutiae of one's research that one looses sight of why one is doing the work. This is especially true, I think, in Archaeological science, where the pursuit of the more esoteric aspects of science may somewhat confuse and obscure the archaeological aims.

My starting point is very simple. The determination and study of the composition of ancient coins is another tool by which we can increase our knowledge and understanding of the past. As such we should feel obliged to attempt to squeeze as much information as possible out of each artefact excavated, employing as many diverse disciplines as possible (see Tite 1972). This aim should, of course, be pursued whilst retaining the artefact's integrity as much as possible (any analysis should alter the artefacts appearance and composition as little as possible). However, this should not involve considerations of a market value, as is often the case with the analyses of coins and other 'portable' antiquities. Indeed, the subservience of sampling strategies to the willingness of assorted collectors and museum curators to 'sacrifice' coins to scientific analyses is one of the possible sources of inaccuracy in recent work.

The problem as I see it is that if we are to exploit the archaeometallurgical potential of archaeological metal artefacts in general, and coins in particular, we need to be certain that the analytical data we retrieve, by whichever scientific technique we chose (or are constrained) to employ, is truly representative of the metal used to fabricate our ancient artefact. Representative is used here in the sense that the sample should reflect, as much as possible, the alloy created in

antiquity. This appears simple enough on the face of it, however, there are many considerations which need to be addressed.

What I set out to do is to investigate the potential of archaeometallurgical investigation of copper-alloy coins for answering some basic archaeological and numismatic questions. To do this it has been necessary to re-evaluate the applicability of certain common analytical techniques, and the way in which they are applied. It has also been necessary to investigate further the changes suffered by certain complex copper-alloys over archaeological time, and how this can affect the accuracy of the results obtained by specific analytical techniques relative to the interpretation of the archaeology.

Until relatively recently the majority of compositional analyses of Roman coins have been concerned with the fineness of the silver (and gold) denominations (for example von Bibra 1873; Reece 1965; Walker 1976). Those base metal analyses which were conducted, such as those by Caley (1955) and, more recently, by Carter (1971), have attempted to look at trends in certain major and minor constituents, such as tin, zinc or nickel, with a view to establish groupings corresponding to provenance, economic or historic events, striking sequence or technological change.

Probably the most travelled path in the compositional analysis of Roman coinage has been that concerned with the argentiferous copper or billon coinages of the mid-third to mid-fourth centuries AD. Various workers have used the analyses of the radiate coins of this period to chart the economic fortunes of the Roman Empire (Burnett 1987.113; Cope 1977a) and study the differing alloying practices from mint to mint (Cope 1969). Indeed, several studies have been solely concerned with the determination of silver in the copper-alloy coins; for example the works of Ravetz (1963) and Barrandon et.al. (1977). Determination of fineness (silver content) has maintained its high profile due to its obvious economic and historic/archaeological significance. However, it has also been established, for example by Cope (1968) that certain other compositional elements were controlled in a similar manner. The lead and tin, for example, in the folles of the Tetrarchy (first quarter of the fourth century) were found by Cope (1968.138) to have been added to the alloy as a 50:50 pre-mixed component. Significant differences dependent on mint were also found between the alloys used for 'radiates' of Claudius II (268 -270 AD.) (Cope 1969).

It has only been since Caley's work in the 60's that sufficiently reliable analyses have allowed investigation of minor and trace elements in coinage alloys. Many of these, unfortunately, consist of so few analyses that meaningful conclusions are impossible, although several researchers have offered interpretations.

Interesting work was carried out by Carter and King (1980) in their investigation of the compositions of the copper-alloy coinage of the period AD 34 - 66. In this study x-ray fluorescence (XRF) was used to analyse relatively large numbers of early Imperial copper-alloy coins. The aim of the project was to,

> "...show that differences in the chemical composition correlate with the date of issue, mint location and in some cases with the ore source." (Carter and King 1980.197).

It was demonstrated that differences in the trace-element (antimony, silver, lead, nickel, iron and tin in these coins) composition of coins of the Julio-Claudian emperors appeared to be related to their date of issue, and that the orichalcum issues of Claudius and Nero have a different trace element profile to that of the copper issues. It was also established, unsurprisingly perhaps, that the contemporary copies had a markedly different trace-element profile from the official coins.

The same year also saw the publication of a similar piece of work (Ovari and Gegus 1980) dealing with trace-element characterisation of mid-third century silver 'radiates' (antoninianii). In this project thirty-four coins were analysed semi-quantitatively by laser-micro-spectral analysis and the presence or absence of certain elements in certain concentration bands and ratios were then established. This information was then used to characterise the products of the mints of Rome and Antioch, and also to support the existence of a third mint, probably Viminacium, the products of which had previously been confused stylistically with those of Antioch.

Both these projects are good examples of the sort of work and the sort of questions which can be answered with full compositional analyses of Roman coins, however, the authors of both recognise that,

> "In our view the question cannot be answered unambiguously because the small number of coins analysed does not warrant far-sweeping conclusions." (Ovari and Gegus 1980.39).

Carter and King (1980.157) go on to say of their ninety-six analyses that, as they span a period of over forty years, the individual chronological groups of coins,

> "...tend to be too small to permit statistically valid inferences to be drawn" (Carter and King 1980.157).

Both these points amount to the same thing; that the sample size dictates the degree of confidence that can be attached to any such programme of elemental analysis.

Furthermore, in order to attach significance to minor variations in the concentration of trace elements, it is necessary to be as rigorous as possible in sample preparation as well as analytical technique. If the aim of the exercise is to look for groupings of coins at very low concentration levels then it is crucial that what variance is observed should be demonstrably a function of the *original* coin's alloy. This thesis will show that this is not always the case, and that often an over-simplified methodology is applied to often highly complex material. The usefulness of a more rigorous analytical and statistical approach is also demonstrated in addressing some of the problems surrounding the production and use of coinage in Roman-Britain, and how this can

relate to, and, hopefully illuminate, aspects of the archaeology of mid-third to mid-fourth century in this province.

1.1.1 Numismatic Application.

The period chosen to supply material for this study is that of the endemic copying of Roman coins from circa A D.270 - 360, and is one where careful and appropriate archaeometallurgy is badly needed. In fact as far back as 1972 attention was drawn to part of this problem by Harold B. Mattingly, who said that,

> "Analysis could also be applied profitably to the fascinating 'barbarous radiate' coinage of Britain and Gaul from the period c. A D.270 - 84...." (Mattingly 1972.325).

The 'barbarous radiate' coinage is one of three major copying epidemics occurring predominantly in Britain and Gaul from about A D.270. All of these pose large problems for the archaeologist and numismatist and the whole period is obviously an area where detailed compositional analyses could shed further light, especially if conducted in concert with more traditional numismatic approaches.

1.1.1.1 The Radiate period.

The first of our three 'epidemics' is that of the 'barbar ous radiates' - so-called because of the spiked crown worn by the emperor which is so characteristic of their official prototypes. These coins are generally regarded as having started in Britain towards the end of the reign of Victorinius (A D.268 - 270), although a date of ^{c}A D.263 is suggested for the continent (Davies 1986.117). The latest prototype so far identified is a coin of Probus (A D. 276 - 282) (Boon 1988. 129). They occur as site finds and in hoards mostly in Britain, Gaul and Germany, but copies of Claudius II's posthumous issues are also known from Italy, Spain and Africa.

The motivation for these copies is now generally regarded (Reece 1987.20) as the local answer to the state's failure to produce low value coins (small-change) in sufficiently large quantities to meet the demand of a rapidly monetizing economy.

Perhaps one of the most puzzling things about this issue is the great variety of size and quality that appear to exist together. Some copies are very well produced and can only be distinguished by the trained eye, whereas some are produced on such small flans, and/or are of such vernacular workmanship, that they could never have been mistaken for the official issues. The hoard of radiate copies from White Woman's Hole (Boon 1988. 129), for example, consisted of issues which fluctuated between 0.19 and 0.91 grams in weight. Other finds can weigh as much as, if not more than, the issues that they were copying (up to 2.9 grams). Furthermore, although many of the types are produced from well-cut dies, many are by no means attempting to be exact copies of their official prototypes. To what extent, therefore, were these really 'copies', and how far can we assume an intent to deceive?

It would appear from hoard evidence, for example, that the aim of the copying was to produce as much coinage as possible from limited metal sources. The White Woman's Hole hoard consisted primarily of copies struck on blanks cut from official coins, four copies from each. Boon (1988.129) suggests that, as the copies bore the same general designs as the larger official coins (and copies), that they,

> "...must have been in all likelihood regarded as of equal value with the larger originals."

The Sprotborough hoard (Mattingly and Dolby 1982) contained radiate copies of similar small size, but these had been produced from pellets of metal cut from a cast rod. However, the analysis of one pellet and one blank showed a silver content of 1.5% and a tin content of 3.5%. both of which would be consistent with the official coins. Unfortunately the analysis is not complete enough to enable the suggestion to be made that the copies from Sprotborough were made from melted down (as opposed to cut-up) official coins, or that an alloy of specific fineness was being prepared.

It has been suggested that the reduction in size occurred gradually over the ten or so years of production (Boon 1988.129), with the larger copies being melted down and re-coined as smaller copies (Minims). This is, however, documented for only two hoards, from Coygan, S.W.Wales (Boon 1967), and White Woman's Hole, Mendip (Boon 1988.102). This may reflect local practices rather than a universal decline in size over time. Indeed, module size may equally well have been dependent on the local availability of suitable metal. The overriding concern of the 'copier' being to produce a given amount of coin from metal of a certain value.

Furthermore, it also seems from the hoard evidence (Boon 1988) that all sizes of coin circulated together. This indicates that the denomination in general (antoninianus, radiate or whatever one prefers to call it) was so over-tariffed that it could be represented by any sized piece of metal. This automatically begs the question; does the composition vary with module size? The copies struck from cut quarters of official coins would, in all likelihood, have contained the usual 1% silver or so, whereas those of larger size would not. Is there a compositional difference which might make up for the lack of size? or were they, as Boon (1988) suggests, purely token coins, their composition being irrelevant. Indeed it is interesting that the Sprotborough copies also contain silver although they were struck from blanks of a prepared alloy (Mattingly and Dolby 1982.31). The issue is further complicated by the fact that they were copying an ostensibly silver denomination, which would have had a silver coating during its circulation. Boon suggests that the copies,

> "...when issued...would in all likelihood have been plated, however speciously." (1988.129).

This is another archaeometallurgical question which has not yet been investigated. The Meare Heath hoard is reported to contain a number of pieces which may retain signs of some sort of white-metal coating (Davies 1986.109), although no analyses has been conducted to date.

Recent work by Davies (1988) has demonstrated the sheer diversity of types and degrees of competence encountered in this series. The surprisingly small number of die-links identified suggest that the amount of this coinage in circulation (especially given the duration of the 'epidemic') must have been enormous. Nevertheless, it has been possible for Davies to suggest 'style groups' based on the few positive die-links and other stylistic grounds. There also appear to be different patterns of coin production in different localities. Davies demonstrated this by plotting module sizes for two different areas; the south-west and the south-east. It is quite apparent from this that there were very different patterns of production operating in each area (Davies 1988).

The few die-links identified, however, do demonstrate the extent of the contacts during this period. Several cover the whole of the south of Britain and a number of the earlier copies have die-links across the channel in N.Gaul. These are the exceptions; a number of style groups identified by Davies (1988) do seem to be severely limited in the extent of their circulation suggesting, on one level, a restricted local usage, but also that relatively long distance contacts could, and did, occur. Accurate trace-element profiles could obviously assist in the confirmation of style groups, and more general compositional analysis could establish if the various and disparate moneyers were working to any collective (or regional) standards of 'fineness'.

1.1.1.2 The Constantinian period.

The second period of copying concerns the issues of the family of Constantine the Great, and is currently attributed to the period A.D.341 - 6. Constantine's reform of A D.330 introduced a reduced size argentiferous bronze coin (the Nummus) bearing as its reverse type, two soldiers standing either side of two standards and the legend 'Gloria Exercitus' (the glory of the army). Later, in A D.335, the reverse design was altered to one standard, due to a decrease in weight and module size. This type was continued by his sons, Constans, Constantine II, and Constantius II. It is largely this type that is copied, although other types also occur, notably the issues commemorating the foundation of Constantinople in A D.330 and the attendant 'Urbs Roma' type.

It was the suspension of the 'Gloria Exercitus' issues in A D.341, followed by an apparent closure of all the western mints which provided the impetus for this second outbreak of copying (Reece 1987.42). As in the previous periods, an acute shortage of 'small-change' was apparently remedied by certain people taking matters into their own hands (either unofficially or otherwise).

As with the 'barbar ous radiates', these copies vary considerably in size and quality of die-cutting. However, there does seem to be a greater attempt to faithfully copy the original design than is evident with the earlier 'barbar ous radiates'. The copies amongst the hoard of Constantinian coins found in the villa at Bancroft (Milton Keynes) are reported to have been,

"...conspicuous by their small size and very careful workmanship" (King 1981.42).

Until the work presented here, the Woodeaton (Oxfordshire) hoard was the only group of this material which had been analytically studied in any detail (King 1978). This hoard consisted of about 1,550 Constantinian coins of which only sixteen were initially identified as copies. However, King was able to show by the application of X-ray Fluorescence analysis that at least 90 were, in fact, copies,

"The hasty and often careless technique employed in the production of genuine issues in the years 330 - 346 can make it difficult even for the specialist to distinguish copies, particularly when the counterfeits have been well made" (King 1978.45).

1.1.1.3 The *FEL. TEMP.* period.

The last phase of copying is that of the so-called "Fel. Temp." copies (A D.354-364). In A D.348 the most important reform of the currency since that of Diocletian in A D.301 was undertaken and marked Rome's twelfth century. The new base metal denominations, of which there were three, all bore the legend; FEL(ix) TEMP(orum) REPARATIO (The return of better times), and a variety of types, although the commonest and most frequently copied one is that of a soldier spearing a fallen barbarian horseman.

These coins were tariffed at a higher level than the previous issues, as well as being larger and having a higher silver content (around 2.5%) (Cope 1974. 235). Consequently the resultant shortage of low value small coins appears to have, once again, prompted an outbreak of large scale copying.

These copies are, like the majority of barbar ous radiates, less than exact copies and this series is predominantly struck on very small flans (minims). Brickstock (1987) has studied the series in some detail (1987), although he is predominantly interested in their chronology. He regards the series as being largely produced locally, and suggests a number of regional centres; Gloucester/North Somerset; Richborough/Canterbury and the County Durham (Piercebridge?) area (Brickstock 1987.118).

This is an obvious area where compositional analysis could be of use. Trace-element profiles may help to clarify the regional groups and enable them to be tied into differences of fabric and/or style. Brickstock (1987.54) suggests that the considerable variation of flan thicknesses amongst the smallest copies may relate to the use of different alloys . He says that it may be the addition

of lead to the alloy which enables thinner blanks to be produced, assuming that the blanks were in fact cast (Brickstock 1987.54). This argument seems a little specious given that the evidence of the Lydney hoard (Cowell 1992. pers comm.) indicates that the blanks were produced from hammering out pellets cut from a cast rod of alloy. The thickness would, therefore, be determined more by the force of the blows during hammering than by the lead content of the alloy. This does, however, point out the need for analyses, especially given that very little work has been done to date. Brickstock (1987.59) notes only eleven separate analyses since 1916, far fewer than for either of the two previous epidemics.

1.1.2 Statistical Methods.

Sensible and informed use of statistical methods is a painful aspect of this type of research, but cannot be ignored. The problems arising from small, non-random samples have already been mentioned, and the topic of sampling strategies will be dealt with below. It is felt that it is not enough to simply analyse (by whatever method) vast numbers of coins in the hope that something new will be discovered. It cannot be emphasised too strongly that a strategy needs to be defined prior to the commencement of sampling, and that this strategy needs to be directed towards the answering of a specific set of appropriate questions.

This project also employed a number of standard uni variate and multi variate statistical methods to manipulate the data, and these will be discussed more fully in the next chapter. The application of uni-variate techniques, such as the use of descriptive statistics (means, modes and standard deviations etc.), t-tests and analysis of variance are, of course, a basic procedural step. The majority of analytical reports will utilise these as standard, together with graphical displays of the data (frequency histograms, tri-partite plots etc.). Multi-variate techniques, on the other hand, have only really made their presence felt in the field comparatively recently (Carter 1993). Consequently, their use is often seen as experimental, and as statistics itself is something of a mystery to all but the initiated (statisticians), their employment as a matter of course can be viewed as 'overkill'. Luckily, a number of papers have been published recently dealing with the application of these methods to compositional data, and the problems that this entails. It has been an integral part of this project to use these studies (for example Ottaway 1979, Gilmore 1981, Borszeki et al 1983, Baxter 1989) in order to establish a suitable multivariate procedure for the exploration of the coin analysis data.

1.2 The Background.

The chemical analyses of ancient coins is by no means a modern phenomenon. Their examination is mentioned by early writers such as Agricola in the 16th century (Ovari and Gegus 1980.35), although the first reports of actual chemical analyses don't appear until the late 18th

and early 19th centuries (Ovari and Gegus 1980.35). In his doctoral thesis, Lawrence Cope (1974) includes an exhaustive survey of Roman coin analyses up to that date, outlining the different themes and approaches. Consequently, it is felt that only a brief resumé of published work up to that point needs to be included here.

The earliest recorded analyst was Martin Hienrich Klaproth, who published the first quantitative analyses of six first century orichalcum coins in Berlin in 1798 (Cope 1974.85). Thereafter interest in this field increased; in 1834 J.Y.Akerman published the first fifteen essays of early imperial denarii, in 1845 F.Gobel analysed republican bronzes, and in 1852 J.A.Philips published his "Chemical examination of the metals and alloys known to the ancients", a work which included a number of analyses of both silver and copper-alloy coins (Cope 1974.86).

Between c.1850 and 1908 a number of researchers carried out analyses on different aspects of Roman coinage, from republican aes (H.A.Grueber.1904) to Egyptian tetradrachms (A.von Rauch.1857 and 1874) (Cope 1974). In 1908 J.Hammer attempted to gather all these analyses together in one volume, this work consisted of about two hundred Roman copper-alloy coin analyses, and nearly two hundred and forty assays of silver coins. The analyses were listed in chronological order according to denomination or weight and this work became the most complete review of its sort.

According to Cope (1974) all the analyses up to 1908 had consisted solely of the major elemental compositions, little attempt had been made to study the trace elements, or, indeed the microstructures. It was not until 1912 that T.K.Rose first used metallography to suggest Roman minting procedures, and, although further attempts were made by later researchers, these were infrequent and insubstantial (see Cope 1974.87). Compositional analyses was, by its very nature, of varying reliability, one of the most intriguing perhaps, being the work of W.Brambach in 1924 (Cope 1974. 88). In this case, a batch of 216 Constantinian (AD 320 - 330) copper-alloy coins were taken from a hoard consisting of 1,017 pieces. These were then melted down to provide a sample of c.675g which was then analysed and found to contain 1.98% silver. The work of Cope (1972;1974) has since shown that a number of different finesses were in operation during the period covered by the hoard, a fact that such an obviously 'heavy-handed' investigation failed to detect.

Levels of 'fineness' and the ratio of gold to silver were seen as the most important areas of research until comparatively recently. West (1953) looked at large numbers of gold and silver coins covering the more important reigns with a view to establish the relationship between the gold and silver, relating this to known historical and textual events. Unfortunately, little attention was paid to the fact that, not only did the weights of the denarius change, but so did the

silver content. Furthermore, those analytical data which were cited were used without any regard to technique or reliability.

In 1964 E.R.Caley published "Orichalcum and related ancient alloys", a work which looked at the chronological variations in the composition of Roman brasses. This marked what Cope (1974.89) saw as " the dawn of a new era of quality and accuracy in chemical analyses". Indeed, Caley's work was of a previously unparalleled standard, although inevitably not beyond criticism. Perhaps the most important area of potential criticism was that of sampling strategies. The techniques of wet-chemical analysis were well advanced by Caley, but sampling techniques still lagged behind. This lead to many sweeping generalisations being made on the basis of often small, heterogeneous samples. For example, Caley looks at the apparent decrease in the zinc content of early Imperial orichalcum (cementation brass) coins in an article published in 1955. The coins he analysed are un-provenanced, indeed no mention is made of their source, let alone their state of preservation. The quality of his chemical analyses is not in question, yet he goes on to compare his results with those done by people up to 100 years previously. His conclusions, which do no doubt reflect a genuine trend, attempt a greater degree of resolution than the data can sensibly support.

The 1950's and 1960's also saw the increasing interest in and use of non-destructive physical analytical techniques. The potential value of these in the compositional investigation of Roman coins was quickly appreciated, especially considering that, being non-destructive, their employment made museum curators considerably more willing to supply coins for analyses. Consequently a relatively large number of analyses have been conducted since the late 50's using x-ray fluorescence and neutron activation techniques. X-ray fluorescence was by far the favoured technique during the 60's and early 70's, not requiring access to a neutron source, and has enabled a vast increase in the numbers of available analyses.

The increase in numbers of available analyses also made researchers aware of the need for a greater understanding of both sampling strategies and of the limitations of the techniques themselves. Carter (1964) has discussed the need for careful preparation of coins for x-ray fluorescence analysis and has also investigated the problem of differing surface and interior compositions of copper-alloys (1986), a problem of particular relevance due to the nature of x-ray techniques, and one that will be addressed in detail below.

The more recent x-ray fluorescence analyses (XRF) of coins published include Carter's (1971) analyses of early Imperial copper-alloy coins. Bowman, Cowell and Cribb (1989) also published an interesting study by XRF of alloying trends in medieval Chinese 'cash' coins. This

investigation showed how a well conducted analytical programme can yield significant results as well as being cognisant of the analytical limitations of the technique employed.

Other standard instrumental methods of analysis, such as Atomic Absorption and Neutron Activation, have also come to the fore during the last fifteen years or so, partly due to increasingly reduced costs, but also due to improved micro-sampling techniques (Szonntagh 1981).

In a survey of numismatic research between 1978 and 1984 Cowell (1986.1024) points out that Atomic Absorption (AAS) was the most frequently used instrumental chemical method for coin analyses during that period. This technique is capable of great accuracy at much greater speed, and using much smaller samples, than the traditional wet-chemical methods of Cope and Caley. Furthermore, the wet-chemical methods require a considerable degree of skill for reliable results and are therefore much more operator dependent (Cowell 1986.1022). If compared with XRF, it is apparent that both techniques can produce acceptable levels of accuracy whilst doing comparatively little damage to the coins. However, Craddock et al (1980.55) state that Atomic Absorption has a number of advantages over XRF. Firstly, by using a sample of drillings taken through the cylindrical edge of the coin, a representative section of all the potentially different regions within the coin is obtained. Secondly, the technique is much more sensitive, being equivalent in this respect to wet-chemical methods. Finally, when analysing a large number of similar samples, atomic absorption can be considerably quicker. Consequently this technique is still frequently used in numismatic research.

Over the last ten years other instrumental techniques have begun to be introduced. In particular Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). This technique is broadly similar to AAS in that it requires a small sample in solution and has high precision for major components and good sensitivity for trace elements. Where this technique has been seen to have an advantage over AAS is in its ability to analyse a wider range of elements simultaneously, however it is still necessary to calibrate the instrument with standard solutions in a similar way to AAS. Recent work conducted between the Institute of Archaeology (AAS) and Royal Holloway and Bedford New College (ICP -AES) has demonstrated that both methods have their advantages and disadvantages and that neither can as yet be regarded as superior for this sort of research (Merkel 1993. pers comm.).

Pioneering work using ICP-AES has been conducted in China by Notsu, Sano, Tominaga and Mabushi (1979,1982 and 1983)) on groups of Asian copper-alloy coins. The work has, however, been conducted from a strongly 'hard' science perspective, with the results receiving little or no archaeological or numismatic interpretation. Perhaps the most useful result of this batch of

analyses has been reported in the paper by Sano and Tominaga (1982). This work looks at the effects of the different constituent elements in copper-alloy coins becoming segregated during cooling/solidification after casting. Although dealing with Chinese coins, which were produced by casting, the results are nevertheless relevant to other coinages (such as Roman) where the blanks were first cast before being struck.

In this study the ICP analysis looked for ten elements (Cu, Pb, Sn, As, Fe, Sb, Zn, Ni, Co and Mn) in samples taken from sixteen separate locations on each of eight coins (four of bronze, four of brass). On comparison of the results it was found that the tin-bronze alloy exhibited considerably greater variation of composition between the sixteen points than the coins of brass. Furthermore, each of the four individual coins could be clearly distinguished by plotting the values of two correlated elements against each other, iron and tin for the bronze coins and iron and nickel for the brass coins.

On the assumption that the variation recorded is the solely the result of segregation during cooling, and has not been significantly affected by post-depositional factors (which is not reported), then an important issue is raised. Any analytical technique which does not involve the destruction of the whole coin, and which produces consistent results for brass coins will not necessarily do so for bronze coins. This has particular relevance for the application of 'non-destructive' techniques' to limited areas (say the edge of a coin), especially if the resultant data is intended for statistical manipulation where the isolation of small variations in trace elements can be regarded as significant.

A program of ICP-AES analysis has also formed the basis of an analytical survey of late-Roman to late-Medieval copper-alloy metalwork in England. This work, by Dr.Nigel Blades (Royal Holloway and Bedford New College), employed ICP to study the development of alloying practices over this very long time scale. The work made use of ICP's rapidity to produce results of good sensitivity and precision and has addressed questions concerning the introduction and widespread adoption of brass, re-cycling of scrap, and the uses and functionality of different alloys (Blades, Bayley and Walsh 1992.9).

Another technique which has recently been applied to the study of ancient coins is Proton Induced X-ray Emission Spectroscopy (PIXE). This method involves the excitation of a sample to emit x-rays in a similar manner to x-ray fluorescence (XRF), however the x-rays are here induced by the use of a proton beam, in this case 3 mm in diameter. The x-rays emitted are then counted by a detector and the resultant spectra analysed by a computerised system in a similar fashion to XRF or EPMA. The authors report the advantages of this system as rapidity for multi-elemental analyses of elements combined with high accuracy and sensitivity (Oeconomedes et al.

1989.348). It is, however, just another surface analytical technique with all the attendant pitfalls, despite being regarded as 'non-destructive'.

Indeed, the work referred to here, although yielding interesting results when compared within the group, must be treated with some caution if the results are to be regarded as absolute values. Furthermore, although the authors recognised the problems of what they term the 'patina' (347), they regard it as satisfactory to strip the coin ultrasonically with 30% formic acid. This process reportedly results in a 4% reduction in the coin's weight and is calculated to mean the removal of 150 μm of surface (348), although how is not stated. It is entirely possible that, despite being organic and therefore less agressive to metals, the acid would have re-deposited copper on the stripped surface of the coin and that, given the likely porosity of the alloys, internal penetration would have resulted in the leaching of certain trace components[1] (Fe, Ni, Ag, Zn, for example). Furthermore, on the basis of work discussed later in this thesis, it is arguable as to whether the removal of 150 μm is sufficient to allow a representative bulk analysis. The depth to which post-depositional alteration can occur will be determined by variables unique to the individual coin and determined by the nature of the burial environment, cleaning procedures and the metallic structure of the coin itself.

Despite the above criticisms, the results are interpreted in a numismatic context and the data are not used to support hypotheses that their numbers do not allow. It is, however, notable that the employment of these so-called 'non-destructive' analytical methods is still in fashion, despite the fact that doubt can be expressed as to the value of the resultant data. It is also an interesting reflection on the numismatic/curatorial community that chemical stripping can be regarded as 'non-destructive' whereas the drilling of a 0.6 mm hole into a coin's edge is still frowned upon and regarded as unacceptable.

Work utilising the established techniques of AAS and XRF has continued to be conducted, often with increased attention being paid to procedure. Of particular relevance to this study is the work, mentioned above, of Cathy King on the hoard of mid-fourth century coins found at Woodeaton in Oxfordshire (King 1977 and 1978). This involved the application of ED-XRF to analyse 350 copper-alloy coins the aims of which were:

1) To study differences in alloy between the issuing mints.
2) To study any significant changes in alloy between AD 330 and AD 341.
3) To investigate any differences in the alloy composition between the locally produced copies and the official issues.

The limitations of the technique are, for the most-part, taken into consideration with the lead values not being converted to a percentage because of the problems of segregation and "subcutaneous" corrosion effects (1977.91). The silver values are also seen to be problematic, all

[1] A pilot study by the author has shown that certain trace elements do, indeed, appear to be leached out of copper-alloy coins during agressive cleaning with formic acid (see appendix 1).

being consistently higher than those determined by wet chemical methods and recorded by Cope (1977.91). This is, however, attributed to the fact that, for some reason, the figures were not corrected to include the tin and lead values, later on it is suggested that surface enrichment may also have a part to play (1977.95). The problems associated with both sets of analyses will be discussed in a later section.

The conclusions of the research can be divided into two parts; firstly the questions pertaining to the official coinage - those of alloy differences between mints and between issuing periods - are not answered satisfactorily. The resolution of the data is not sufficient to enable clear cut distinctions to be drawn, and what attempts are made can only be regarded as tentative suggestions. What is meant by this is that, due to the limitations of this 'surface' analysis technique (when applied to this type of material) the necessary sensitivity and precision are not achieved. These values can therefore only be regarded as semi-quantitative. These limitations are taken on-board by King, who says that,

> ".....there is no doubt that individual results obtained by wet analysis are undoubtedly more accurate for the coin as a whole than those obtained by superficial analysis....." (1977.86).

Where this work makes a significant contribution to the archaeology of Roman-Britain is in the discovery that the copies have a markedly different composition to their official prototypes. Indeed, King states that,

> " It is by their alloy content that the imitations can be most readily distinguished from genuine issues" (1978.45).

This means that the only possible way to confidently identify a coin of this period as the product of an official mint is by its composition. King, herself a highly respected numismatist, reports that,

> "Style is the most difficult criterion on which to separate the genuine from the imitation folles in this period, particularly since a small but significant group of the copies are of high quality and reproduce legends and mint marks fairly carefully while official issues are often of inferior technique" (King 1978.45).

What the application of XRF to this material has demonstrated is that the copies from Woodeaton contain virtually no silver, very little tin and large amounts of lead. For this purpose it matters little that King's (1978) results for the official coins give silver values of 1 - 1.6% and Cope's gives 0.8 - 1.2% (Cope 1974.226-7). What is important is that the silver values for Kings copies are consistently below 0.8% (the vast majority being below 0.6%). The same is true of the tin values; Cope's three recorded results range between 1.98% and 3.85%, although only one result (2.41%) is from a coin issued in the west (the other two are from Constantinople and Alexandria respectively). King's XRF analyses for tin are largely between 1.5% and 2.5%, whereas the copies are mostly under 1.0% (1977.100). Consequently it is not necessary to achieve great accuracy in order to establish this sort of general trend. It is with the study of the products of different mints that considerable accuracy is required, both in instrumental detection and in ensuring that the analysis is conducted on a truly representative and 'virgin' sample.

The importance of King's (1978) findings to the archaeology of Rome's north-western provinces is potentially of considerable significance. Not only does this have serious ramifications for the published ratios of copies to official coins in hoards and site finds, but also for our interpretation of the motivation behind the production of the copies.

Two issues immediately present themselves: do the copies and the official issues form the same part of the coinage ?; and if they don't, how do we explain the fact that they are generally such good copies? The make-up of the Bancroft hoard (Milton Keynes) suggests strongly that, not only must the copies be largely contemporary with their official prototypes, but also the fact that both issues were hoarded together indicates that they circulated together (King 1981.46).

King states that although the compositional distinction between the copies and the official issues is clear....,

> "....what is less certain is whether some of the imitations were made from official coins which had been melted down and their silver and tin extracted" (1977.97).

Reece (1987.43) suggests that the removal of the silver from the coinage alloy of the copies anticipates the same move by the central administration around A D.356 and recorded in the Theodosian Code[2]. This would presuppose some sort of semi-official status being attached to the copies, perhaps issued by the magistrates of the civitas capitals, in order to allow for the continuation of commerce and payment of taxes. This is, of course, hard to substantiate. Nevertheless, accurate and representative compositional analysis, especially trace-element profiles, could begin to identify groups of material and their probable source.

Another large scale analytical program was published by Zeigler in 1983. This had similar, although less clearly defined, aims to those of King's study. This project used WD-XRF to analyse a very large number of mid-third century copper-alloy coins which came from a hoard found at Brauweiler in Germany (Ziègler 1983). In this project a great deal of care was taken to prepare the coins for analysis and in developing a method to analyse what was seen as the 'whole' coin. Unfortunately a number of assumptions were made concerning the nature of the alloy analysed resulting in the analyses being only a very general approximation of the coins original composition. Nevertheless, because the surface of the coins was removed mechanically the degree of accuracy was sufficiently improved to allow a meaningful comparison to be made between the issues of different mints and issuing authorities (1983. 91). This work will be discussed in greater detail in chapter four, however, it should be mentioned here that the work is indeed an important contribution to the study of the coinage of the period.

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[2] Codex Theodosianus 11 21,1 (AD 371): "Not only shall the bronze called dichoneutum be immediately delivered to the treasury, but it shall be entirely withdrawn from use and circulation and nobody shall be allowed to possess it publicly". The term 'aes dichoneutum' is taken to mean the the argentiferous copper-alloys used up to 355/6 (Burnett 1987.137).

An interesting discovery of this investigation of particular relevance to the current project concerns the analyses of the contemporary imitations (so called 'barbar ous radiates') and of the issues struck in the name of the 'Divine Claudius', after the death of that emperor (in AD 270). The radiate copies (as we shall be calling the 'barbar ous radiates') from the hoard exhibit the same range of quality that one would expect for these coins. Compositionally the analyses show some interesting trends. All the forty-two copies analysed apparently contain the merest trace of silver, apart from one which contains an amount suggesting that it may have been either over-struck on, or made from, a contemporary official coin. What these coins do contain are significant proportions of zinc or tin, and it is interesting that, almost without exception, if one element is high, the other is low. The possible significance of this in the light of results from this project will be discussed in chapter 3.

The analyses of the 'Divus Claudius' issues are remarkable in that they appear to corroborate a historical event. Analysis reveals that, like the radiate copies, a large number of these coins contain virtually no silver (Zeigler 1983.76). According to Zeigler (1983.93) the literature refers to the illicit activities of the influential mint official ('rationalis'), Felicissimus. This character incited a mint workers revolt shortly after the accession of Aurelian, allegedly because he feared that his tampering with the coinage would be found out. The analyses show that, during Felicissimus' office, inferior (silver-less) coin had been issued, whether directly by the mint itself, or by 'private' operation which Felicissimus had tolerated. After the revolt had been suppressed the mint of Rome was temporarily closed. It is suggested that it was due to the complete loss of confidence in the currency for which this incident was partly responsible that Aurelian undertook a complete reform of the currency in AD 274.

An associated technique to XRF has been employed by researchers in Eastern Europe with a similar degree of success. This is laser-micro-spectral analysis and its variants. The technique consists of firing a low power laser beam at the sample area (the edge of the coin) to atomise a small amount of the metal, this is then analysed via a spectrometer to give a spectral readout (Ovari and Gegus 1980.39). The technique is somewhat similar to Optical Emission Spectrometry (OES) in that it is the light energy emitted by a spark discharged through the evaporated sample which is analysed. Consequently, the same problems associated with any 'surface' technique apply.

The composition of copper-alloy issues from the Kingdom of Bosporus (the Crimea) was investigated by Michail Triester (1988) using a variant of this technique. This is another in depth survey, covering an immense time scale - from the fourth century BC. to the fourth century AD. in just 87 analyses. Consequently, he is only able to look for general trends in his data. These only require a limited degree of accuracy, and one which his technique is capable of supporting.

What Triester does is to isolate nine alloy types on the basis of the ratios of the components. This alloy type is defined by the presence of tin, lead and zinc at a level of either above or below 1%. This means that only the more drastic corrosion engendered surface alterations are likely to affect the attribution of the coin to any given alloy group. It is possible that the lead may well be corroded out from the surface layers to such an extent that the difference between the surface and interior lead concentrations is considerably greater than 1% (see chapter 4), and the same is also possible, in extreme cases, for the zinc content (Cope 1972.12). Nevertheless, given that the alloys are defined by a combination of more than one element, it is likely that the groupings are largely authentic.

The main aim of this study (Triester 1988) is to map the chronologies of the different alloy groups and to discuss the likely reasons for the many varied changes that occur at different times. Many of the changes can be attributed to known historical events, or if not to actual events, then the reasons for an alteration in alloy type can be ascribed to a known (or hypothesised) set of circumstances. For example, it is suggested that the sudden change in 80 BC. to a 'pure' copper coinage, an event which has no precedents in the Hellenistic period, was the result of the economic isolation of the Bosporean kingdom caused by the Roman-Pontus wars (Triester 1988.14). The trade in the Pontus basin in the 60's BC. is known through historical records to have been paralysed as a result of the wars which lead to a cessation of imports of the alloying components (Triester 1988.14).

Another study which used this method was that of Ovari and Gegus (1980). This is a particularly important piece of research, not because of the technique, or even the results, but because of the logic behind the work. As mentioned in the general introduction, this project used a 'surface' technique semi-quantitatively to establish the presence or absence of certain elements in given concentration bands. This information possessed sufficient patterned variation to enable the products of the mint of Rome and the mint of Antioch to be defined dependent on the presence of zinc at levels estimated at about 1% and above (1980.39). It was also possible to suggest that some coins, numismatically classified as Antiochene, are the products of a third mint, as their composition differs significantly from both that of Antioch and Rome. It was a stated fact that,

> "...the major aim of this investigation was to find a certain significant element (or elements) and not to present a full, accurate, quantitative analysis." (1980.38).

Furthermore, it is also recognised that a compromise has to be reached between the amount of damage inflicted on a coin in extracting an 'adequate' sample for analyses and the reliability of that analyses. Because one of the stated aims of the project was to be 'non-destructive' (1983.38) the absolute accuracy of the analyses would be compromised,

> "It should be noted that the elements listed can be considered present *in the estimated ranges*, because of the compounded effects of the lack of suitable standard samples, the

> local inhomogeneity of the samples caused by the inadequate early smelting technologies, and the alteration of the alloy composition in the soil due to corrosion and diffusion." (1980.39).

This example illustrates some important points which are often not mentioned in published analyses. Whether or not the researchers are themselves aware of the limitations of their techniques and the results they obtain, it is important that these be adequately communicated to the archaeological and numismatic community. This is something that is only recently starting to happen. The dangers lie in the interpretation that the results are given by the archaeologist/numismatist/historian. It is all to easy to use such data to support a favourite numismatic theory because, after all, this is incontrovertible scientific fact, is it not? The scientist knows that this is not so, but the numismatist may not. The definitive numismatic history of the Roman coinage issued by gallic mints during the fourth century (Depeyrot 1982), for example, states that, in the issues of AD. 330-348,

> "...the lead is 6% to 10% at Trier, but 8% at Lyon and Arles...." (Depeyrot 1982.75).

However, these results are taken from King's XRF analyses (King 1977) the limitations of which have already been discussed. Furthermore, the problem of leads' insolubility in copper-alloys at levels over 0.002-0.005% (Cope 1972.14) is well known to archaeometallurgists, with the result that wide variations in lead content are expected in the values from any analytical method. Indeed, the AAS analyses of similar coins by the author produced lead values from 5.34% to 13.46% within ten coins of the same issue from the same mint (see chapter 4).

These factors will be investigated further in the appropriate chapter, however, an increasing awareness of these problems is evident in the literature. Ovari and Gegus (1980.37) criticise the majority of published analyses up to that year for not having, or omitting to discuss, a numismatic aim. One paper published by Caley (1956.285) is cited as presenting some interesting analyses of a certain class of coin, however little could be done with the results as the coins were merely described as bearing the name of the emperor Trajan Decius. Luckily, more recent work has tended to involve the collaboration of both numismatists and scientists as well as the growing recognition of the existence of a hybrid specialist, the archaeometallurgist.

This sort of collaborative research has already been mentioned in the paper published by Bowman, Cowell and Cribb (1989), this is a collaboration between two scientists and a specialist in the archaeology/numismatics of the material investigated. Another example of this sort of collaboration is the paper by Cowell and Murray (1980) which again combines the appropriate interpretation of well conducted analyses with a suitably measured numismatic commentary.

Another area of recent collaboration has been between the materials scientists and the statisticians. This also represents a major advance, enabling considerably more information to be extracted from analytical data sets. A paper by Stos-Fertner et al. (1977) attempts to utilise a

battery of uni-variate techniques to investigate compositional traits in Arabic Dirhams. This article makes some important points concerning sample size and the meaning of 'statistical significance' as well as stressing,

> "....that a rough evaluation of data resulting from the analysis of the chemical composition of coins is insufficient and can lead to false conclusions. Only a statistical analysis of the data can lead to an authoritative statement..." (1977.192).

This is an assertion that the present author would also like to emphasise. It is especially important that any noted differences or similarities in data be quantified and that a rigorous and, above all, consistent set of criteria be established against which the data can be measured.

Much of the more recent work has been concentrated on establishing guidelines for the multi-variate statistical investigation of all types of compositional data. This type of statistical method is regarded as particularly suited to compositional data in that it uses all the variables simultaneously. Papers by Ottaway (1979), Schwabe and Slusallek (1981), Gilmore (1981), Borszeki et al. (1983), Krause (1989), Baxter (1989) and Evans (1989) discuss the use of cluster analysis and other multi-variate techniques to interpret compositional data. Some of the papers look at a variety of materials (Baxter looks at glass composition, Evans at pottery composition), Ottaway investigates the use of cluster analysis to group bronze age artefacts by their elemental profiles, and then tests the validity of the clusters by another statistical technique, discriminant analysis. The results are readily explainable by the known archaeology and the clusters are very clearly defined. This is, perhaps, a saving grace because the data analysed have been gathered from a variety of sources, and are the products of a number of different analytical techniques. Had the groupings been defined by small differences/similarities in trace elements, then it would have been possible to suggest that the differences were the result of the differing limitations of the various analytical techniques employed.

Both cluster and discriminant analysis are multi-variate techniques utilising a number of compositional elements simultaneously to define groups exhibiting similar characteristics. The methodology behind their application in archaeometallurgy will be discussed in chapter 2. Morven Leese (1981) discusses the statistical reasoning behind the adoption of multi-variate techniques and also the dangers inherent in using any statistical method to support the archaeological interpretation of compositional data .

In the paper by Krause (1989) compositional data were again gathered from a variety of sources and analysed by cluster analysis. The findings demonstrate that the metal composition changed chronologically and the ways in which it changed lead on to some interesting questions concerning the origin of certain classes of artefact. However, the use of data produced by a number of different analytical techniques (OES, NAA and wet chemical analyses) automatically lead to criticism, especially where differences in trace element concentration are concerned.

Schwabe and Slusallek (1981) looked at the application of cluster analyses to compositional data from three different archaeological materials (glass, ceramic and metal). Of interest to this study is the investigation of 547 separate analyses of Egyptian bronze artefacts, all of which were analysed by AAS on the same machine. The material spanned a vast time period (from the Late Dynastic period through to the end of the Roman period) but was, nevertheless, able to distinguish the artefacts on the basis of their function. It is of interest that, given the very long time span represented, the artefacts are grouped more according to their function than their chronology. Furthermore, if the elements are divided into two groups; those major components which would have been controlled by the artisans, and those minor/trace components which could not have been controlled and which are impurities relating to ore source and smelting technology, then different clusters are obtained. The suggested reason for this is that it is the controllable components only which reflect the desires and traditions of the crafts people alone. The minor components obey a more natural order which has not been knowingly tampered with by man.

More recently the use of Principal Component Analysis (PCA) has become popular as an alternate method of investigating the structure of compositional data sets. In particular the work of Baxter (1989a, 1989b, 1989c, 1991, 1992, 1993) has dealt with the problems surrounding not only the successful application of PCA to compositional data, but also to more general aspects of compositional analyses. His work, in collaboration with other specialists, has looked at the application of PCA to analyse medieval glass compositions (Baxter and Heyworth 1989, Baxter 1991), but his findings are generally applicable to any set of compositional data.

Baxter has also been a central figure in the debate surrounding the use of Aitchison's loglinear contrast method. This is an important contention from a background point of view, consequently a general overview will be given.

Both clustering methods and PCA are normally carried out on raw data or on data which has been transformed in order to standardise variability. However, recent research by Aitchison (1986) has criticised the use of this approach for compositional data on statistical grounds. The problem centres on the fact that "...any vector x with non-negative elements x_1,....., x_d representing proportions of some whole is subject to the obvious constraint, $x_1 + ...+ x_d = 1$." (Aitchison 1986.1). This 'unit-sum constraint', he argues, means that standard multivariate techniques ought not to be used on data which sum to 1 or 100%. In order to overcome this problem Aitchison advocates a 'log linear' transformation of the data prior to PCA . However, Baxter (1989,51) notes that the technique has problems with data sets containing zero s and that it is overly sensitive to small values, results being dominated by those variables with a low presence (Baxter 1991.40).

More recent papers (Tangri and Wright 1993) accuse Aitchisons method of adding...,

> "...spurious structure to the table of data, thereby producing distorted results." (1993.111)

which has lead to suggestions that users would be better off going back to using standard PCA and putting up with whatever distortions result from that. However, Baxter is less critical of the method and in a reply to the Tangri and Wright article (1993) states that the method is still useful for providing insights into data whilst advocating care in its use and suggesting that it be used as only one of a selection of data exploration tools.

Discriminant analysis has been mentioned above as another tool for assessing structure in compositional data. This method is the inverse of cluster analysis or PCA in that the groups in the data are stated and the analysis provides an estimation of the likelihood that, on the basis of the data alone, their attribution is correct. This method is therefore often ideal for investigating compositional variation in artefacts which can be grouped archaeologically. Coins can be grouped by issue or mint by the numismatist and then this attribution can be checked against the coins chemical composition. The application of this technique to these types of data was discussed by Carter and Frurip (1985), where XRF analyses of 245 copper Quadrantes of Augustus were subjected to this technique. This pioneering study used the XRF determinations of Fe, Ni, Cu, Ag, Sn, Sb and Pb together with the physical measurements of the coins to confirm the suggested chronology for these issues.

A further application of this method was published by Carter this year (1993). This paper uses discriminant analysis to confirm the attribution of sixty-nine copper Asses of Augustus (27 BC.- AD 14). These coins were apparently struck in three two-year periods by three different moneyers. Carter found that the trace element compositions changed sufficiently drastically from year to year for discriminant analyses to accurately confirm the chronology of the coins proposed on purely numismatic grounds in Roman Imperial Coinage (Sutherland and Carson 1984).

Carter also co-authored a paper comparing the results of different analytical methods (Carter, Caley et al. 1983). This is of particular relevance to the present study, as will become clear in future chapters. Eight orichalcum (cementation brass) coins which had been analysed gravimetrically by Caley in 1964 were analysed again by WD-XRF, ED-XRF, Radioisotope excitation, EDT-XRF, NAA and AAS. The results were then compared.

The general conclusion was that good agreement was reached between the different methods, but that variation did exist. WD-XRF analysed a layer only 5 μm thick, although this did not seem to introduce unacceptable error. However, it was noted that...,

> "...concentration gradients in coins at and near the surface appear to occur only in certain *highly alloyed* coins; in these coins differences will obviously occur between XRF determinations and analyses made by other methods." (1983.203).

Where more difference was noted was with ED-XRF, here the possible effects of concentration gradients was acknowledged (204). For NAA it was also noted that problems were caused. This time by heterogeneities in the metal structure. This lead to errors of ±10% for zinc and ±20% for gold and arsenic. Carter sums up by saying..,

> "...it is necessary in analysing such objects by XRF to prepare the specimens carefully, and even then errors are sometimes unavoidable due to composition gradients extending inwards from the surface." (1983.212).

He also adds that even with methods which analyse the entire object (such as NAA or wet-chemical), it is possible for the presence of a non-representative particle to introduce unacceptable error.

It is for the reasons stated by Carter, amongst others, that many workers prefer, if possible, to use a method where internal metal samples are taken. Such a method is, of course, AAS, and it is the application of this technique to archaeological material (especially metals) which is the topic of a joint paper published back in 1976 (Hughes et al.). This paper lays down standard procedures for AAS and cites the expected detection limits for the commonest elements. There is a section dealing with the analyses of copper-alloys, and it is this which has formed the technical basis for the majority of projects involving the AAS analysis of copper-alloy artefacts, including the present study.

This section deals, albeit briefly, with sampling strategies and the problems of heterogeneity (1976.22). It then discusses the difficulties of getting the sample into solution, and once achieved, how to keep it there. Tin is often problematic, requiring gentle heating, although the article fails to deal with the problems associated with argentiferous copper-alloys. This was a problem encountered during the present study, and will be discussed in detail in chapter 4. What this article does emphasise is the necessity of matching the calibration standards with the sample solutions as closely as possible. This is particularly important for copper-alloys; there being a significant enhancement of the absorbence signal emitted by most elements in the presence of copper (as much as 10% for some elements). The importance of making use, as much as possible, of standard reference materials (SRM's) is also stressed. These are specially prepared alloys of carefully controlled composition, and as such can be used to check the calibration of the instrument. The authors report that such SRM's were used to check the accuracy and reproducibility (precision) of the method with very good results.

The general trends in the published literature are quite clear; there is a growing appreciation of the limitations of the various techniques available, the need for communication between the numismatist/archaeologist and the materials scientist is largely recognised, and the employment of statistical methods in both sampling strategies and especially in data exploration has become a normal practice. What is still generally lacking is an appreciation of the degree to which post-

depositional modification (including conservation) can effect a copper-alloy coin, and that these effects vary considerably between alloy types. Carters assertion that...,

> "...accurate analysis of most roman coins may be obtained using XRF provided that the coins are cleaned properly." (Carter 1983.203)

was based on a comparison of techniques conducted on relatively homogeneous cementation brass coins. Unfortunately this statement appears to have been taken by some to mean any copper-alloy coin. This is decidedly not so, as the paper by Sano and Tominaga (1982) demonstrates.

Furthermore, the degree of accuracy required is obviously determined by the questions for which the analysis is designed to answer. With the application of multi-variate statistical methods it becomes increasing important that the data are as reliably accurate as possible. In order to do this a deeper understanding of how the environment can affect our analytical data is required. Much has already been published describing how these processes work (Condamin and Picon 1964, 1972, Charles 1973, Chase 1979 for example) but little has been done to relate these effects to archaeological material in a meaningful fashion. Tylecote (1979) published a paper where the degree of corrosion suffered by an archaeological copper-alloy was related to the soil type (pH etc.). However, little attention was paid to the fact that the soil conditions are likely to have altered considerably (and frequently) in ways that are unlikely to be discernible. What is readily apparent in this study is how varied even the visible effects can be, and also how severe. One artefact is observed to be de-stannified to a depth of 0.5mm. Certainly a broad correlation exists between soil type and degree of corrosion, acidic soils are generally more corrosive than alkali soils, and peaty soils are generally benign due to the protective action of polyphenols (copper containing enzymes). Yet beyond this blanket assertion little has been done. It is important to understand which elements are affected more than others and in which combinations. It is also important to understand generally how the more complex copper-alloys used in ancient coins behave in the burial environment, and how this data can be used to ensure that the correct analytical techniques are employed in their analysis. Only then should the resultant data be examined for structure by multivariate techniques with a view to establish accurate and meaningful elemental profiles.

Chapter 2:
Sampling Strategies and Analytical Technique

"...our current preoccupation with, and uncritical reverence for, the past, is a disease rare in history." (Reece 1985.62)

2.1 Sampling Strategies.

2.1.1 Population and Sample Size.

The question usually asked at the outset of any project which involves analysing a section of any given population, is "how big should the sample be?". This is really not the first question; what needs to be asked initially is, "what are the questions that this project is going to address, and how do we go about obtaining a sample which will enable us to do this?". Once we have established this base-line we can begin to talk about numbers, but *not* percentages (see Shennan 1988, chapter 14 for a discussion of this). The question only then becomes "what size of sample is required which will *adequately* represent the whole". The 'stock' answer obviously involves the standard formula which derives a numerical value from considerations of the observed data variance within the pertinent observations (see Snedecor and Cochran 1976. 58 and Stos-Fertner et al 1977). This is, or should be, the accepted procedure and therefore discussion of this is assumed to be superfluous to this discussion. The considerations here concern the initial stage of sampling; the choice of a sample 'suitable' to furnish the answers to the particular questions posed.

A 'suitable' sample is one which has been designed to yield answers of a specific type or quality. Three main questions need to be born in mind when formulating this design, each relating to important considerations of interpretation: is the sample archaeologically meaningful?, will it give statistically valid results?, and will it be sufficient for a reliable chemical analysis? Obviously such questions can exist on different levels. The archaeological considerations usually involve the sampling of a given population of existing excavated material, which is itself a sample of the total population that exists or once existed. The fact that the existing portion of the original population was, in most cases, not randomly selected (the very fact of survival into the present may have been limited to material of a particular composition for example) is a fact often overlooked, and will inevitably bias our surviving population. Given this far from satisfactory situation we need to make the best of the population that exists and that involves the use of both archaeological and statistical knowledge to extract a sample which preserves the archaeological

structure of the original group in a statistically meaningful fashion. It seems to be a recurrent fact that studies of this nature frequently take a small, un-representative sample of archaeological material, divorced from it's context, and then treat it as if it was a metallurgical sample derived from industry (for example Notsu and Mabuchi 1979 or Caley and McBride 1956).

In selecting the coins analysed for this thesis different sampling strategies were adopted for each hoard or group depending on the particular set of objectives (questions). The only general rule was that sufficient data were available for a meaningful statistical evaluation. Stos-Fertner et al. (1977.200) suggest that any attempt at representativity is highly questionable in groups comprising of less than twenty coins, and that larger groups be analysed if possible. Wherever possible a figure of thirty analyses for each group was aimed at, in some cases (The Wallbottle hoard for example) the group was so diverse that a larger sample was deemed appropriate. In other cases, the Richborough hoard specifically, it was necessary to analyse the entire group of seventy-three coins in order to satisfy the aims of the project. Some coins within groups were also selected because of their poor visual condition and degree of corrosion, some were selected because of their clean and un-corroded state.

What is advocated here may sound uncomfortably like Shennan's definition of a 'Judgmental' sampling strategy (1988.300), and therefore subject to the same criticisms. However, it is felt that this is the more appropriate method for the stated aims. Indeed, Shennan himself regards the main point of criticism of this approach as,

> "...not that the estimates resulting from it may be distorted, but that we have no means of evaluating the representativeness of the sample selected other than through an evaluation of the selector and our own knowledge of the substantive situation." (Shennan 1988.300).

However, Shennan is using as his starting point the problems surrounding the sampling strategies applicable to the excavation of archaeological sites. The strategy we are discussing is rather different; one which is applicable to the sampling of assemblages of coins and the selection of these assemblages. It is not regarded as important to this study to quantify our sample in any but the crudest terms. As Shennan himself states....,

> "Whether such aggregate measures are of interest to us in any given study depends on our *aims*." (1988.301)

It is apparent that the overall aims of this project are significantly different from those requiring a 'probabilistic' sampling strategy. Only where a sample is required to be representative of a particular group of material has 'probabilistic' sampling been required, such as with the Fenny Stratford hoard (see section 3.1.2.2).

This project also differs in several crucial ways from most previous studies which have involved the analysis of coins . Firstly, all the material analysed in this project comes from well documented hoards. This means that each specific group studied consists of coins which have

been subjected to the same burial environment. Furthermore, each of the groups discussed here have been selected partly because the reports of their discovery record that they were recovered from inside 'sealed' containers. This factor suggests that the material will have been protected from the worst ravages of the surrounding environment (see individual case studies in chapter 3 for details). Two groups of material, however, were selected precisely because they did not come from protected environments. The coins from Richborough (Chapter 3.2.3.1) were selected to answer specific questions concerning the effects of corrosion on one particular type of coin for which good comparative material was available. The Market Deeping site finds (Chapter 3.4) were selected because they represent a spectrum of coin types commonly encountered on British sites. The spectrum also includes issues from the periods of endemic copying, for which good comparative material is also available from the hoards. The burial environment was also quite harsh, the site being in the Fens and therefore peaty and acidic[3]. This, therefore, provides an example of a selection of coin types which have been subjected to one of the more severe environmental conditions liable to be encountered.

> Previous studies, on the other hand, have used material which, in most cases, was obtained...,
> "...through the generosity of a number of numismatists and museum authorities..."
>
> and which was acquired.,
> "...at random and mainly un-provenanced." (Cope 1968.118)

This obviously means that any analysis which involves statements based on comparisons between coin compositions must assume that either no modification of the composition has occurred, or that it is at least uniform and therefore not dependent on the nature of the burial environment. As Tylecote (1979) observed, this is patently not the case,

> "...a reasonable relationship appears to exist between the pH of the soil and the state of the metal. Acid soils are aggressive to metals and alkaline soils are benign." (Tylecote 1979.345)

Consequently, in order to ensure the quality of material analysed in this project it has been necessary to exercise a degree of 'judgement'. This has also been true of the strategy adopted in sampling the individual coins from within the hoards. Again, sampling was conducted with specific questions in mind, thereby making the application of true 'probabilistic' sampling inappropriate. The sampling strategy adopted for each group of material will be discussed further in the relevant chapter sections.

2.1.2 Representativity and the considerations of micro-sampling.

Sampling technique is of also of considerable importance when deciding upon the area of each individual coin from which to take samples. Cope (1972) considers the problems of internal corrosion and segregation in relation to wet-chemical analysis, and uses this as a point in favour

---

[3]Shreer (1977) reports on a National Bureau of standards (U.S.) test where two types of copper and ten types of copper-alloy were exposed for up to fourteen years to fourteen different soil types. The results gave the most corrosive types as being; peat (pH 2.6), cinders (pH 7.6) and tidal marsh (pH 6.9).

of wet-chemical analysis over micro-analytical techniques such as those advocated for use with Atomic Absorption (Cope 1972,13). Carter (1964) has done the same for XRF, concentrating on the problems of surface alterations caused by environmental alteration and segregation, although, as already mentioned, has concentrated only on the simpler copper-alloys. However, Charles (1973) suggests that the only *reliable* way of obtaining a representative sample is by taking drillings from a number of positions on the artefact. It is the latter view which is taken in this thesis, the reasons being discussed below.

The inherent heterogeneity of ancient metals, and copper-alloys in particular, has been discussed at length elsewhere (Caley 1963, Carter 1978, Charles 1973, Chase 1974, 1979, Condamin 1964, 1965, Cope 1972, Hall 1961, Szonntagh 1981, to name but a few) and although it is a subject largely beyond the scope of this thesis, it's fundamental importance requires it to be considered in part.

Heterogeneity in copper-alloys can be caused by any one, or a combination of, several factors, these can relate to either the internal nature of the alloy itself, or to external factors. They can be listed as follows:

1) Segregation of the different components during cooling.
2) Corrosion.
3) Inadequate or partial melting of the components.
4) Poor mixing of the components.

Of these, it is the first two which are consistently the most important and require further discussion.

2.2.1 Segregation

During the solidification of a complex copper-alloy of the type discussed here, the different components will separate out. These then form distinct 'phases'; sub-alloys in the case of the moderately soluble components or, in the case of highly insoluble components, such as lead, discrete phases of metal rich in that component. Consequently this 'phase separation' means that the *precise* composition may vary according to sample size and where within a coin a sample is taken. The obvious remedy would be to conduct an analysis of the entire piece. This has been done. However, given the relative rarity of most archaeological metalwork, and the need to preserve material in as complete a state as possible to allow investigation by the other sub-disciplines within archaeology, this is seldom possible. Cope advocates the use of half a coin (1972.13), and it is on this basis that he regards traditional gravimetric analysis as being more representative than analytical results from smaller samples such as the 10 - 50 mg used for AAS.

However, experiment also suggests that the use of entire coins (or even half coins) for analysis may not, in any case, supply an answer of sufficiently enhanced accuracy to warrant its

destruction. Cope (1972.16) himself refers to experiments conducted by C.T.Peters, where a simulation was attempted of the alloy used for the reduced folles of the house of Constantine. A copper-alloy was prepared with a composition of 1.39% silver and 12.5% lead, as an approximation of the actual argentiferous copper used in antiquity. The alloy was then cast into a one-libra strip. Peters found that the silver content varied between 1.15% and 1.57% from the start to the finish of a pour of molten alloy, and that the lead content varied similarly, from 10.35% to 14.62%. These effects are interpreted by Cope as being due to both gravitational segregation of the lead in the crucible, and the mutual affinity of lead for silver in copper-alloys (Cope.1972.17).

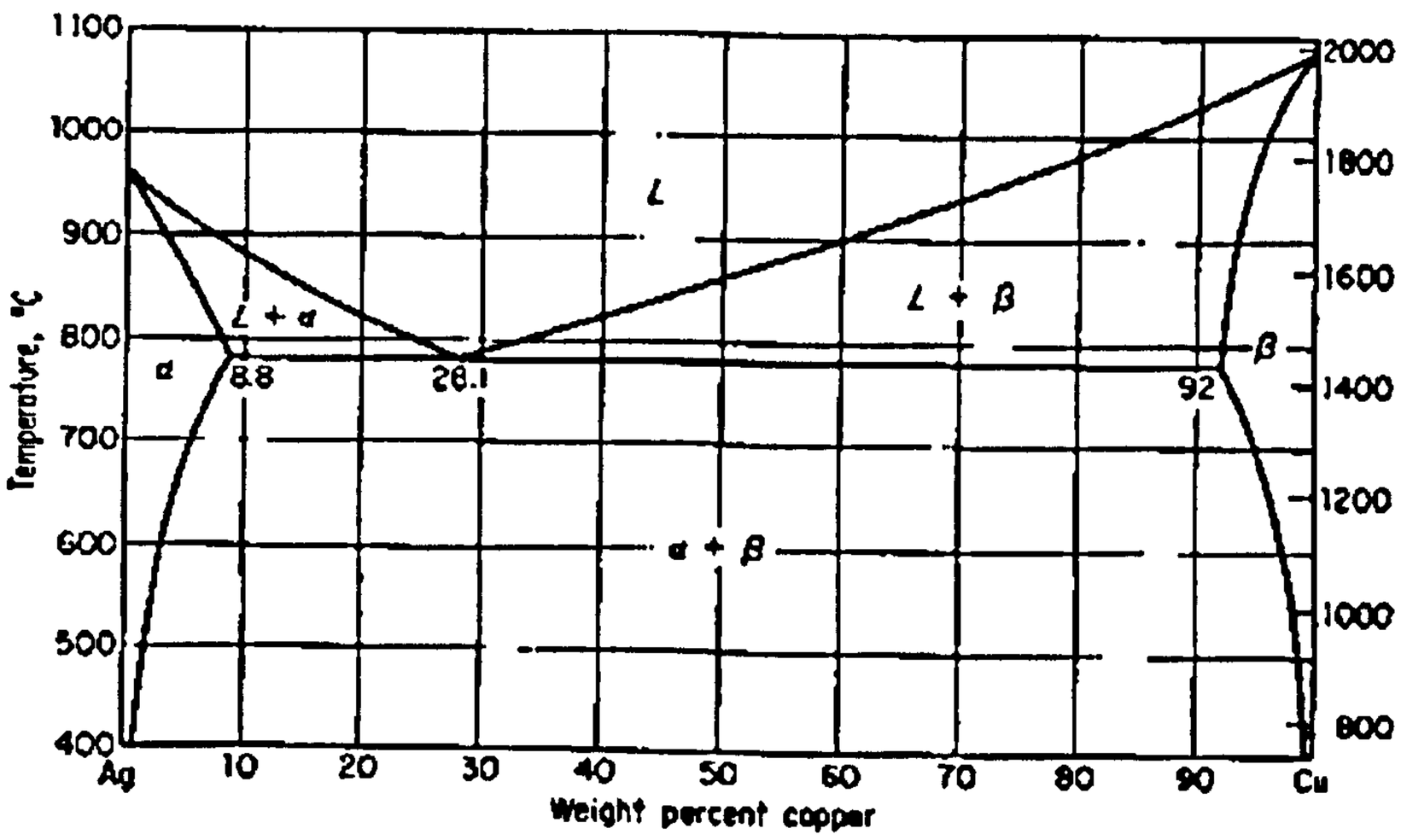


FIG 1. AG-CU PHASE DIAGRAM (after Avner 1988).

If such variation can occur within a one-libra melt of metal prior to the casting of individual blanks, and since further segregation will inevitably happen during the cooling of the blanks when cast, it is not surprising that definitive coin compositions are rare. Philip Tyler (1972.252) concludes his discussion of these problems in relation to third-century Roman antoninianii (radiates) by saying that,

"....even over the limited field of mid-third century Roman antoninianii, the metallic analyses of whole series of Roman coins is revealed as an exercise in approximation even with the most sophisticated scientific techniques now available."

Cope himself, whilst being a staunch advocate of gravimetric analysis, is also aware of the extreme locality of the segregation problems associated with complex alloys. He reports an experiment where two halves of the same coin (a follis of the Rome mint) were analysed separately (1972.17). The results gave a silver value of 1.42% and 1.08% respectively, each of

which correspond to a different theoretical 'fineness' standard postulated by Cope (4 and 3 scrupulae per libra of alloy). Thus, says Cope;

> "...which one is intended by the moneyer cannot therefore, be determined from a single analysis.....but only by statistically significant numbers of analyses of closely dated coins." (1072.17)

The paper published by Sano and Tominaga (1972) further demonstrates the practical consequences of these segregation effects, and shows how the degree of variation within a coin is also dependent on the type of alloy and the differing levels of 'solid solubility'. In copper-alloys the elements most likely to be of interest to us are gold, nickel, zinc, tin, silver, arsenic, antimony, cobalt, iron, chromium and lead, although this can vary from analyst to analyst. The solid-solubility's of these in copper differ greatly, and are given in Table 1.

a) Unlimited	gold	complete mutual solubility
	nickel	complete mutual solubility
b) Partial	zinc	about 25% at 210°C, rising to 39% at 454°C and decreasing to 32.5% at 902°C.
	tin	1.3% at 200°C, rising to 11% at 350°C and 15.8% maximum in the range 520-586°C.
	silver	0.2% at 300°C, rising to 8.0% at the eutectic temperature of 779.4°C; eutectic, 71.9% silver.
	arsenic	6.9% at 200°C.
	antimony	2.5% at 250°C, rising to 10.4% maximum at 645°C.
c) Slight	cobalt	negligible solubility below 500°C, rising to 5.1% at 1110° C.
	iron	0.01% at 500°C, rising to 4.0% maximum at 1094°C.
d) Minute	lead	almost insoluble; about 0.002-0.005%.

TABLE 1. LIMITS OF SOLID SOLUBILITY IN COPPER (after Cope 1972.14)

These characteristics can be displayed graphically, in the form of a phase-diagram. This will also furnish information about the likelihood of different phases forming containing varying amounts of the alloying components. For example, a phase diagram can tell us at above which percentage of an alloying component (the'solute') the metal starts to consist of more than one phase (in a binary alloy system). This information can then be related to the metals structure (through optical microscopy), and can be used to suggest the percentages of alloying elements present. However, a phase diagram is presenting the processes of cooling and solidification under ideal or 'equilibrium' conditions. These were seldom, if ever, attained in antiquity. Equilibrium conditions, strictly speaking, are those in which there will be no change with time, however, they can be approximated by extremely slow heating and cooling in controlled

conditions (Avner 1988.155). Consequently, caution must be applied in relating the ideals of a phase diagram to the realities of archaeological metal.

Segregation can exist at two levels; macro-segregation and mechanical displacement segregation. Macro-segregation arises from the different levels of solid solubility, however, the extent of this is determined by the solidification history of the metal (Charles 1973). In essence we have a situation where a liquid rich in solute (the alloying component) is formed due to the level at which mutual solubility can be maintained, this is then rejected ahead of an advancing solidification interface towards the center of the mould (Charles 1973.109) (Fig.2.).

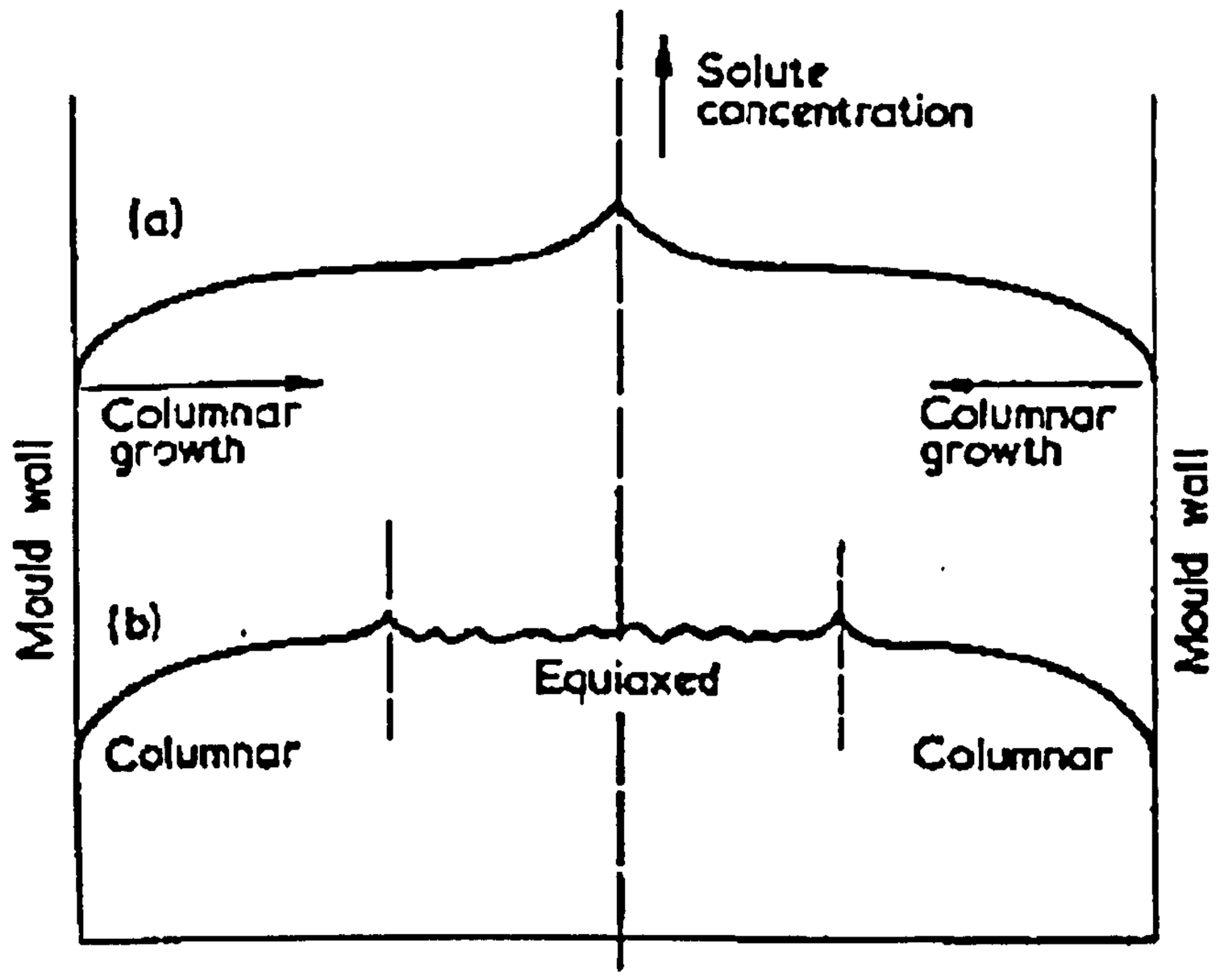


FIG.2. NON-EQUILIBRIUM FREEZING OF ALLOY IN MOULD (AFTER CHARLES 1973.109)

With a number of alloying components it is possible to have a number of liquids remaining, rich in different solutes and solute levels, and freezing at different temperatures. This situation can be further affected by the rate of cooling (i.e. non-equilibrium conditions) which in turn affects the rate of freezing. Examples of this 'normal' segregation would be seen in high tin content copper-alloys where a solute enriched liquid of higher density and low melting point is formed. This liquid then segregates into the shrinkage voids left within the solidified copper matrix.

In order to achieve a representative sample it is, therefore, important to know where and how this solute enriched liquid is distributed. In archaeological metal it is often found uniformly

distributed interdendritically or at the grain boundaries. However, this sort of segregation (provided that it is uniform) will present few problems to an analysis conducted on a drilled sample of about 20 mg as used for AAS,

> "...since the drill will produce a mixture of materials from a volume encompasing the whole extent of the heterogeneity." (Charles 1973.108)

Where the problems do become significant in archaeological material is when the macro-segregation is severe and non-uniform. This is often the case, and can be caused by a large presence of a highly insoluble component, such as lead or (above a certain level) tin, by rapid cooling, by 'gravity' or by 'inverse' segregation.

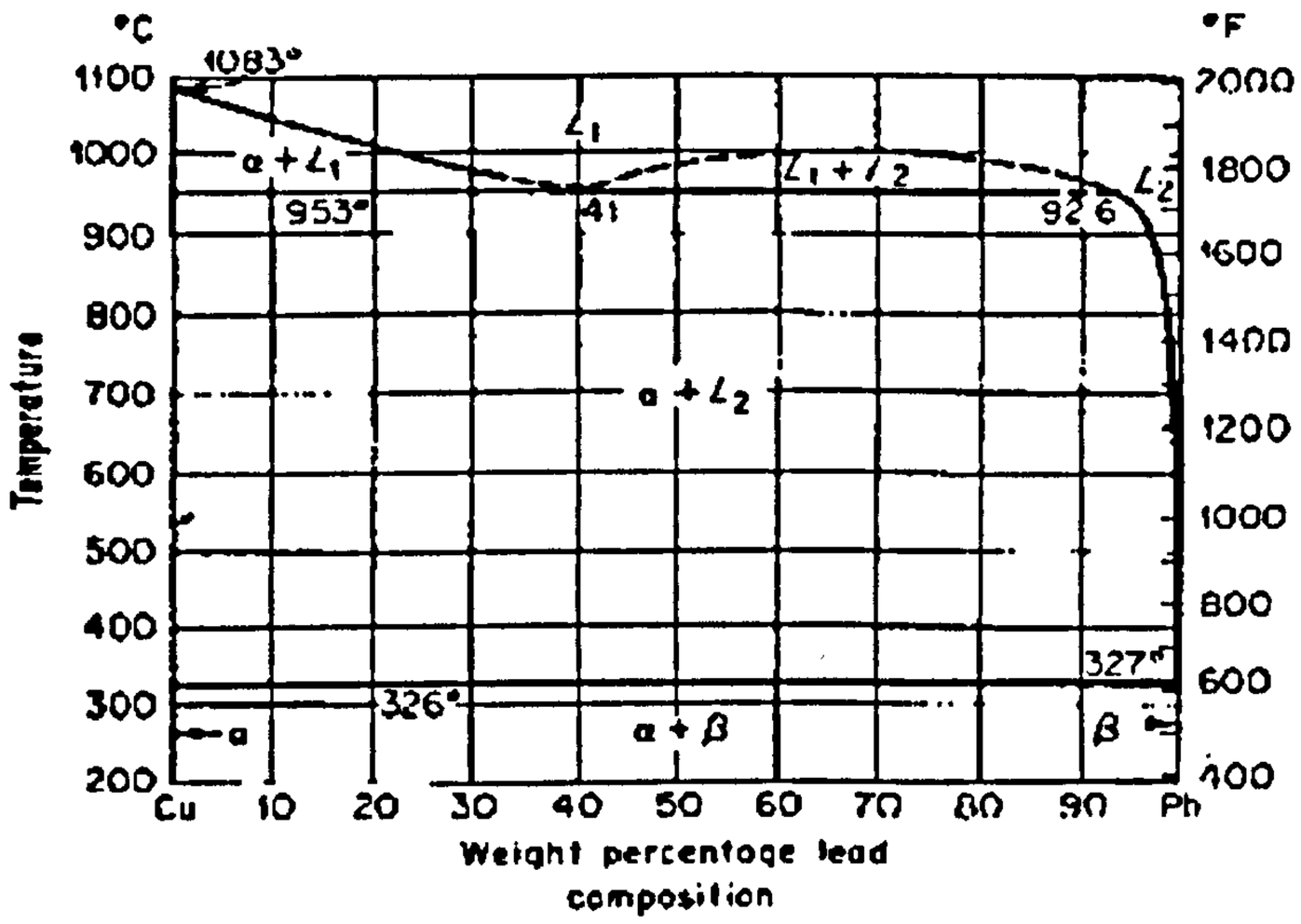


FIG 3. CU-PB PHASE DIAGRAM (AFTER AVNER 1988).

Gravity segregation is caused where a component, or combination of components, are significantly heavier or lighter than the matrix. Charles cites an example (1973.111), where, in tin-antimony based white metals, a tin-antimony compound forms as cuboids. These then float in the molten alloy and separate to the surface. In archaeological metals lead is again the most susceptible component. Being inherantly insoluble, the lead collects as globules whilst the matrix is still liquid, these then tend to settle towards the bottom of the mould or even crucible. This effect is well demonstrated by the results of Peter's experiment cited above.

Inverse segregation occurs as a result of the interdendritic segregation common to archaeological metals; as solidification occurs the dendrites are gradually formed. These are long crystals which extend towards the walls of the mould, which shrink as they solidify. This shrinkage is caused by the change in specific volume from liquid to solid and creates a vacuum which 'sucks back' solute enriched liquid outwards to the mould wall (Charles 1973.112). An example of this is 'tin-sweat' in high-tin bronzes, where the expulsion of tin-rich liquid to the

surface of the alloy creates a white-metal 'sweat'. A more common example found amongst archaeological metal is where the same effect is applied to highly leaded alloys. This can be seen in the EPMA distribution map for lead in a leaded-copper-alloy coin of Theodosius 1st (A D. 379-395) (Fig.4).

FIG.4. LEAD DISTRIBUTION MAP OF A THEODOSIAN LEADED-COPPER COIN

Further segregation can also be caused by the high temperature working of the alloy subsequent to casting. This is mechanical displacement segregation, and involves the displacement of a lower melting-point phase during working. For example, a grain boundary phase, such as a silver-copper eutectic, may well be liquid at working temperature and consequently squeezed out to the surface. The hot-striking of coins would be capable of achieveing this effect, and may be partly responsible for the severe segregation of certain constituents (especially lead and tin) found in coinage alloys.

2.2.2 Corrosion

If all the above problems weren't enough, the situation is further complicated by the affects of corrosion. This can effect both the surface composition, by surface enrichment/depletion, and the bulk composition, by diffusion. Surface effects in the simpler, more homogeneous copper-alloys are relatively easy to overcome by careful sampling procedures, as discussed by Carter (1964). Diffusion can be more problematic, the commonest types in copper-alloys being de-zincification

(of orichalcum) and de-stannification (of bronzes). Contrary to some opinions (Ziegler 1983.88, for example), these effects may extend to a considerable depth (especially in porous alloys). Furthermore, these processes often do not leave any obvious corrosion products entrapped within the metal. This is because the aqueous corrosion environment responsible for the removal of zinc or tin from the alloy does so by a chemical replacement process which re-deposits copper that has been previously taken into solution (Cope 1972.12).

Furthermore, the results of the work conducted for this thesis strongly suggest that the effects of the corrosion of highly segregated alloys can lead to considerably increased heterogeneity. This is evident both within a single coin and between similar coins suffering from different degrees of corrosion. This work will be discussed in chapter 4, together with the serious ramifications that this has for the employment of 'non-destructive' analytical techniques in certain classes of alloy.

Corrosion is a complex process consisting of a number of physio-chemical phenomena which cause a metal to be damaged by external agents (Marchesini and Badan 1979). The mechanisms behind these processes have been the subject of a number of publications (Scott 1985, Marchesini and Badan 1979, Leoni 1979, Organ 1977, Wranglen 1972, Tomashov 1966, etc.) and the reader is referred to these for a detailed discussion. However, it is felt that a general overview of the relevant aspects of the processes involved is appropriate.

The process of corrosion can be seen as the reversion of the forcibly purified metal to a more stable form as a compound.

The commonest corrosion phenomena, and those which are of concern here, are electrochemical by nature, involving the presence of an electrolyte which is in contact with the metal. This electrolyte is usually an aqueous solution, often the ground-water of an archaeological site. This can be either acidic or alkali, and this form of corrosion is generally known as 'wet-corrosion' (Marchesini and Badan 1979.200).

These corrosion phenomena can be simplified to two levels; a widespread, uniform 'all-encompassing' surface corrosion or a localised pitting corrosion. The localised corrosion can either be the result of the corrosive processes' preference for particular morphological aspects, or for specific constituents of the material. Morphological aspects which favour corrosion include such features as workhardened areas and breaks or cracks on the metals surface. These can then become, given the right conditions, self perpetuating pits or craters of active corrosion. Of particular interest to this study is the selective corrosion of specific constituents, especially in the light of our discussion on segregation.

The mechanism of the wet corrosion of metallic artefacts in general is dependent on two major factors. These are thermodynamic factors and kinetic factors;

1) Thermodynamics:

These are the physical factors which combine to produce certain corrosion effects. Free energy can be related primarily to electrochemical processes. These essential factors are; the dissimilarities in the electrode-potentials of the component metals; the ions present in the surrounding electrolyte (the burial environment in this instance); and can also include pH and temperature.

The more electro-negative metal in an alloy will displace a metal less active from solution in the surrounding electrolyte. This occurs because the two metals are connected electrically by an electrolyte between them; whether as a sub-surface layer or as a liquid permeating a porous metallic structure. In this 'electrolytic cell' the more electro-negative metal will go into solution and corrode. Thus zinc displaces copper in solution leading to the leaching out of the zinc from the alloy (dezincification) and the redeposition of copper. Some of the other metals which occur in archaeological copper-alloys have the following electrode-potentials;

System	Electrode potential E_0 (V)
$Au/Au^{3}+$	+1.50
Ag/Ag+	+0.799
Cu/Cu+	+0.521
$Cu/Cu^{2}+$	+0.337
$H^{2}/H+$	-0.00
$Sn/Sn^{2}+$	-0.136
Pb/Pb^{2}	-0.126
$Fe/Fe^{3}+$	-0.036

TABLE 2. ELECTRODE POTENTIALS OF SOME ELEMENTS COMPARED TO THE HYDROGEN ELECTRODE. (after Marchesini and Badan 1979.202).

The nature of the electrolyte can, however, affect the behaviour of the component metals. The presence of certain non-metallic ions such as sulphate or chloride can affect the corrosion process to a considerable degree. The corrosion potential of a soil is often related to its resistivity; low resistivity reflecting the presence of moisture and soluble salts (= ions from a source other than the artefact); thus a soil of low resistivity is liable to be more corrosive than a soil of high resistivity (Wranglen 1972.63).

Even at the thermodynamic level it is apparent that reliance upon the standard electrode potentials of the participating metals can be misleading. The so-called galvanic series is an attempt to remedy this, consisting of specific series of metals and alloys relating to specific electrolytes. Comparison of these shows how much the relative electrode-potentials can alter. For example in a 3% salt solution (NaCl) silver, copper, nickel, and lead all have their electrode-potential reduced (i.e. become more electro-negative and prone to corrosion), but titanium and aluminium are ennobled by, in titanium's case, more than 2V (Wranglen 1972.70).

2)Kinetics:

Kinetic factors are those which control the rate and degree of corrosion. Where thermodynamics can suggest the end products of a corrosion reaction, kinetics defines the rate of that reaction.

Corrosion inhibition is a kinetic factor, and is often the result of the build up of insoluble corrosion products on the anode of the corrosion cell. However, porous oxides or redeposited metal can actually increase the rate of corrosion; this is especially true when the artefact is exposed to alternating wetness and dryness (Avner 1988.587). Another form of corrosion inhibition, this time electrochemical, is over voltage, notably hydrogen over-voltage. This effect can inhibit corrosion velocity in acidic environments and is dependent on the build-up of hydrogen atoms on the electrodes of the corrosion cell.

Temperature is another largely kinetic factor. Although perhaps not directly relevant to archaeological material, it is worth noting that, as an example, zinc corrodes considerably more rapidly at 60 - 70^{o}C (Wranglen 1972.92). Of more direct relevance is soil depth; this can reduce the replacement of oxygen to the reaction, consequently slowing (or in totally anaerobic conditions, stopping) the reaction. However, this effect can be offset by the presence of sulphate reducing bacteria (Devibrodesulphuricans), which can increase the corrosion velocity considerably.

Thus it must be understood that metals can behave in a variety of ways during burial. The processes of corrosion are dependent upon a number of complex factors which need to be seen as a totality interacting with each other. Neither thermodynamic nor kinetic factors can be viewed in isolation; the corrosion reaction is a product of both.

It would therefore seem to be important to understand to what extent the burial environment can affect the composition of copper-alloy coins, and how sampling strategies can minimise these effects. Certainly with the major components of coins collected from a variety of sources, a variation of say 1% may represent different post-depositional factors rather than an

archaeologically significant difference. The problem must be equally valid with trace-elements; certain elements such as iron, may migrate into a coin through voids or cavities left by inter-granular corrosion, equally, some may migrate into the surrounding soil matrix.

Factors of this kind need to be considered before analyses conducted on coins from different sources can be satisfactorily interpreted in the ways suggested by Carter (1964) and others. In particular, where multivariate statistical methods are employed as a means of grouping coins purely on the basis of their compositions, it needs to be established that such variation is not a result of environmental factors.

Because of the complexity of factors, discussed above, which contribute to the corrosion of copper-alloys it is not possible to predict the effects of a given environment on a particular alloy, especially as that environment is likely to have altered over time. Consequently an empirical approach is felt to be appropriate; analysing material from selected sources.

Too little attention has been paid to this aspect of study, which must call into question the validity of much published material. This must be particularly relevant where a surface analytical technique has been used to investigate trace-element compositions.

Carter and Kimiatek (1979) studied the differences between surface and interior compositions of Roman copper-alloy coins with particular reference to XRF. He states that he could discern no significant variation between the surface composition and that of the interior (Carter and Kimiatek 1979). However, it should be pointed out that they used either relatively pure copper coins (quadrantes) or simple copper-zinc alloy coins (sesterces), both of which are significantly more homogeneous than the highly leaded tertiary or even quaternary alloys employed in the later coins used in this study. As Sano and Tominaga (1972) demonstrated, it is obviously incorrect to infer that Carter and Kimiatek's findings are equally applicable to other types of copper-alloy coins. Furthermore, all four of their copper quadrantes came from the same burial environment (the silts of the river Tiber), whereas the histories of the four sesterces are unknown.

Other work which has looked specifically at the effects of corrosion on compositional analyses includes Condamin and Picon (1964, 1972), Cope (1972), and Chase (1979). Condamin and Picons' articles in particular look at the effects in both silver alloys (1964) and copper-alloys (1972). Both papers stress that these effects can be severe, and that care needs to taken in the choice of analytical technique,

> "...we may then conclude that the changes suffered by coins in the course of time have repercussions both on the results provided by methods of total analysis and on the results provided by methods of superficial analysis." (Condamin and Picon 1972.66)

However, their work does no more than highlight the existence of the problem and suggest reasons for it. It does not look at the extent of the phenomena or its practical repercussions on any given program of analysis.

In the light of these studies of the metallurgical processes involved in coin production, and the changes suffered over archaeological time, it is apparent that the aims and limitations of any analysis need to be clearly defined.

It should be possible with a careful sampling strategy to arrive at a reasonable estimation of an individual coin's present composition. Furthermore, with a sufficiently large number of analyses of carefully selected coins, it should be possible to begin to be able to talk about the composition of the alloy that the moneyer originally intended to produce. To produce these results the sampling strategy must consist of two levels. On one level we have the desire to achieve as accurate as possible an analysis of each individual coin. This requires an understanding of the specificity of corrosion effects to alloy type and environment type, as well as an understanding of the alloys behaviour during the coins manufacture. All these factors must point to a method which involves the chemical analysis of an homogenised sample taken from several locations which are below the level of post-depositional and inverse segregational effects.

On the other level we need to use these individual coin analyses to add to, and hopefully enhance our knowledge and understanding of the culture which produced them. This will involve a sufficiently large sample of individual analyses of similar material to be able to generalise about the compositional traits. We need to ascertain what the 'normal' extent of variation is within a particular group in order to pick out those coins, such as contemporary 'copies', which are 'abnormal'. To do this convincingly we must ensure that the material analysed comes from the same source, and not from a variety of museum and/or private collections. We must be certain that the variation investigated is truly the result of the factors that we wish to ascribe it to.

2.2 Analytical Technique.

2.2.1 Sampling.

In consequence of the factors discussed in the previous sections, it was decided to adopt a multiple sample position strategy, using drilled samples in which the first millimetre or so of material from each hole is discarded. The sample was collected from an average of four holes, placed as equidistantly as possible around the cylindrical edge of the coin. These were then usually mixed-up together to create a homogenised and representative sample of the metal from which the coin was originally made. The drills used for this process were standard high speed

steel (HSS) twist drills, it having been established that any contamination by the drill is insignificant (Hughes et al. 1976.22). The drill size was determined by the thickness and condition of the coin, being either 0.6mm or 0.8mm.

2.2.2 Atomic Absorption Spectrometry (AAS).

The sample of metal produced by this procedure was then subjected to Atomic Absorption Spectrometry (AAS). This technique was chosen for the following reasons;

1) It is an instrumental technique and therefore less operator dependent than the classic gravimetric or titrimetric techniques employed by Cope.
2) It is capable of a similar degree of sensitivity and precision to the classic methods. The detection limits vary depending on the element, from about 0.02% for arsenic to about 0.0003% for zinc (estimates based on analysis of standard reference materials, 10 mg in 25 ml). Precision likewise varies but is estimated at ±1-2% for major components (>1 wt.%), ±5% for minors (1-0.05 wt.%), and ±20% for trace (<0.05 wt.%).
3) Despite the fact that each element is run separately, once a calibration has been set up, the analyses can be run in a relatively short time. The same sample solution can usually be used for the analyses of all elements.
4) Access to the equipment was not a problem, although several necessary repairs required a qualified engineer. This was expensive and involved 'running the gauntlet' of considerable amounts of 'red tape' at the Institute to release the funds, with the resultant loss of time.

In order to use this technique the sample needs to be in solution. The procedure adopted to do this is based on that discussed in Hughes et al. (1976). Approximately 15 mg of the homogenised sample is dissolved in 2 ml of aqua regia (three parts hydrochloric acid to one of nitric), this is then gently heated (60° C) in order to ensure that the tin in fully digested. The resultant solution is then made up to 25 ml with de-ionised water. In most cases it was found that this amount of acid was sufficient to maintain in solution the small amounts of silver present. Where this was not the case two separate solutions were used, one using 10-15 mg of sample in 2 ml HNO_3 only (made up to 25 ml) and one using about 3 mg of sample in a 10 ml solution containing 5 ml of aqua regia. This strongly acidic solution is able to maintain the gold and tin in solution and the HNO_3 only solution will maintain all the other elements in solution, including the silver. During the course of the analytical work presented in this thesis, problems were encountered with the detection of low silver levels by this two solution method, these will be discussed in chapter four.

Once the sample is in solution the analysis needs to be conducted within a few days to avoid inaccuracies caused by the precipitation of tin oxide (Hughes et al. 1976.24) and the possible loss of silver and other elements by absorption on the walls of the container.

Atomic Absorption is a spectroscopic technique which relies on the absorption of light of specific wavelength by atoms in a sample. The instrument consists of a spectral light source (a hollow cathode lamp) which directs a beam of light energy through a high temperature flame at a

detector. The general theory behind the technique is that if a solution containing a metallic salt is aspirated into a high temperature flame, a vapour is formed which contains atoms of the metal. Some of these freed metal atoms may be raised to an energy level which is sufficiently high to permit the emission of radiation characteristic of that element. However, a much larger number of these freed atoms will remain in their ground or unexited state. These atoms are capable of absorbing light energy of a characteristic wavelength and the extent of this absorption is directly proportional to the number of ground state atoms present in the flame. In order to exploit this phenomenon, the sample solution is aspirated into a high temperature air/acetylene flame (2400° K) which frees the constituent atoms. At the same time light energy of a wavelength specific to the element in question is directed through the flame and is picked up by a detector. Consequently any shortfall in the amount of energy received at the detector is recorded and this information is then electronically processed to give an absorbance reading.
Sometimes it is desirable to use a hotter flame (acetylene/nitrous oxide - 3200°K) in order to reduce interferences, as is the case with tin. It was also found beneficial to use a nitrous oxide flame for the determination of arsenic, because, although not achieving maximum sensitivity, the increased stability allows a greater precision and confidence in the values obtained.

In order to utilise the fact that the amount of energy absorbed by the freed atoms is directly proportional to the number of atoms and consequently the amount of element present it is necessary to set up a calibration. To do this a sequence of solutions is prepared containing a gradually increasing amount of the element in question. These are then sequentially run on the instrument and the respective absorbance levels measured. Points are then plotted on a graph of absorbance against concentration and a line drawn through the points to give the calibration curve. This 'curve' should be more or less straight for the best results, although calibrations covering a wide range of concentrations will tend to curve dependent on the characteristics of the particular element. It is then possible for the absorbance of the sample solutions to be read off against the calibration curve to give the concentration in parts per million. This figure can then be converted to a weight percentage by a simple mathematical formula (Hughes et al. 1976.24). The Pye Unicam spectrometer used in this study was interfaced with an IBM clone PC running SOLAR software. This allowed the setting-up of accurate calibration curves for each element, and enabled that calibration to be viewed throughout the analysis. Consequently adjustments could be made when required in order to ensure accuracy.

The standard solutions are made up from either chemically pure 1000 or 10,000 ppm stock solutions (BDH) or from dissolving up selected standard reference materials. Where stock solutions are used it is important that the resultant standard matches the sample solution as accurately as possible, both in acid content and in major components. In particular it is known that the presence of copper enhances the absorbance signals of other elements by as much as 10%

(Hughes et al.1976. 23). In order to compensate for this all standard solutions made from stock solutions are matched for copper by the addition of 400 ppm of copper per 100 ml of solution. Furthermore it was found beneficial to make up 'cocktail' standards containing the same collection of elements as the samples within a copper-rich matrix. Another method is to use standard reference materials (SRM's). These are especially prepared, chill-cast alloys of a certified composition, which are produced by a number of governmental standards offices (notably the French, Canadian and U.S.A. Bureau of Standards). These can be drilled and dissolved in the same way as the samples to provide not only calibration standards but also a method of checking the accuracy of a calibration set up using the stock solutions. Generally good to excellent agreement was achieved between the SRM's and stock solution standards, although certain characteristics of theRoman coinage alloys could not be matched with available SRM's.

In particular the presence of about 1% of silver in most of the coinage alloys investigated was a feature which SRM s were unable to match. Consequently it was necessary to rely on stock solution standard for both calibration and check. Luckily it became possible to use a drilled sample from a medieval brooch containing 0.15% silver as a check. This artefact had previously been analysed three successive times by ICP-AES as part of the work of Nigel Blades (pers. comm.), and consequently provided a useful comparison and check for the AAS. There are, nevertheless, problems inherent in the determination of silver in concentrations around the 1-2% level in copper-alloys by both AAS and ICP-AES. These will be discussed more fully in the light of the current research in chapter four.

2.2.3 Electron-probe microanalysis (EPMA).

This technique was adopted fairly late in the development of this project and was a fortuitous addition to the limited arsenal of analytical techniques available. The technique involves the excitation and chemical analyses of the surface of selected areas on a sample as small as 2-5 microns. Excitation is achieved by directing a beam of electrons at the sample surface and then measuring the intensity of the x-rays generated. In a similar way to AAS, the wavelength of the emitted x-rays is characteristic of a particular element and its intensity is directly proportional to its concentration. This is the basic theory behind a number of related analytical techniques (XRF, PIXE etc.), where EPMA differs is in the fact that the beam is very finely focused to give very accurate quantitative analyses (detection limits in the order of 50-100 ppm). Archaeological applications were soon to be recognised with an article published in 'Archaeometry' as early as 1962 (Hornblower 1962). Unfortunately, the hardware involved is financially restrictive and the degree of technical competence required to maintain and produce reliable results considerably greater than, say, an SEM. Consequently, although the possibilities have been appreciated for a long time, relatively few projects have had the opportunity to use the technique. Indeed, until the installation of the probe in the Wolfson Laboratories at the Institute of Archaeology (London), the

only instrument usually available for archaeological applications in the UK was the probe run by the Research Laboratory for Archaeology and the History of Art in Oxford.

In essence, the technique is similar to scanning electron microscopy (SEM), the principal difference being that in SEM the electron column is designed to produce high quality backscattered and secondary electron images, x-ray analysis being of secondary importance. The electron micro-probe, on the other hand, is primarily designed as an analytical tool using wavelength dispersive detectors. This difference in the overall aim of the instrument results in a variety of significant differences in its construction and operation. In order to achieve accurate quantitative analyses it is necessary to have a large take-off angle between the sample and the spectrometers. To achieve high resolution electron images, on the other hand, it is necessary to have a low spectrometer take-off angle (20-40°). Furthermore, because imagery is its main application, the SEM is designed to examine three-dimensional, un-polished samples which also results in considerable variability in emitted energy intensity. Purely analytical instruments have been designed with a spectrometer take-off angle of 75° (Potts 1987.326), however, because of the necessity of locating the area to be analysed accurately, some SEM ability is desirable. Consequently the take-off angle in most recent instruments is in the order of 40° to 50°(Potts 1987.326).

Because a high take-off angle is a prerequisite for accurate and reliable analyses the sample needs to be extremely flat, smooth and polished. The usual sample preparation method (and the one adopted here) consists of embedding the sample in a block of polyester resin and then first grinding, and then polishing the exposed face. A series of gradually reducing abrasives are employed, ending up with a series of diamond pastes culminating in ¼ micron. An even and regular polish is required as any scratch in the beams path could lead to additional (and unaccounted) absorption of the x-rays emitted (Potts 1987.346). In the same way topography can also have an effect on the level of emitted x-rays detected. A sample which is polished on an angle, or an incorrectly mounted sample block can lead to considerable error in the calculated absorption correction (Potts 1987.346). This is because the correction factors built into the software automatically assume that the sample is flat and that the take-off angle, on which the correction is based, is therefore constant.

The applications of this technique in this project are on two levels. Firstly, in view of the factors discussed in the previous sections, it was felt important to investigate the behaviour of the different constituent elements within complex copper coinage alloys. How severe are the real effects of segregation in archaeological metal? and how does this affect a representative analysis? How consistent are these effects? and how deep do they penetrate? To do this the probe was pre-programmed to scan the beam over a pre-determined area on a series of specially prepared

samples, and to measure the amount of a given element in a specific minute area. These individual readings are then amalgamated by the probes software in a pre-determined fashion to create a compositional 'dot-map' of that particular element. A series of concentration bands are chosen, each band corresponding to a particular emission count level. Each of these bands then has a colour assigned to it resulting in a graphical representation of the distribution of different elemental concentrations.

In order to confirm the validity of the trends shown in the 'dot-maps' a series of individual microscopic points were analysed on a line running from the centre to the outside of the coin. Each point was analysed by a beam 5 microns in diameter, and the series of analyses were placed approximately 100 microns apart. Each point was analysed three times and the mean values were then plotted on a line-graph. The resultant trend could then be compared with the mapped concentration and any purely topographical phenomona identified. In general very good agreement was achieved between the methods, the results of which will be discussed in context in chapter four.

The second level of application was in the investigation of the different visible phases within the overall composition. A variety of inclusions and areas were analysed. Some of the smallest inclusions, however, were impossible to analyse accurately. This is because the total 'excited volume' at the acceleration current used was larger than the volume of the inclusion (see chapter 4.2.1.1). Nevertheless, it was possible to obtain some useful analyses of the larger inclusions both at the surface of the coins and deep within the copper matrix.

2.2.4 Energy dispersive x-ray fluorescence (SEM-EDAX).

An energy dispersive x-ray detector attached to a Hitachi scanning electron microscope was occasionally used for rapid qualitative analyses. For the reasons already outlined, quantitative analyses were not usually undertaken. However, the technique was very useful in gaining an insight into the presence or absence of elements prior to AAS, and also in establishing the presence (above a certain level) of lighter elements undetectable by AAS, such as sulphur.

2.3 Statistical Methods.

Apart from basic descriptive statistics, standard t-tests (Shennan 1988) were used in establishing the level of difference (or similarity) between different data sets. These were conducted on the data in Excel spreadsheets using the t-test option in the data analysis add-in. Where non-standard t-tests were required the more flexible routines in SPSS-PC+ were used.

Multi variate statistical methods were chosen to be the usual method of data investigation after the basic graphical depiction of the different elements present. The methods were chosen in

order to view the data as a whole and in a way that will be sensitive to the interaction of all the different constituents. Problems could obviously arise with the unit-sum constraint issue discussed in chapter one ('the closure problem'). Recent work by Baxter (1992.1993) and Wright (1989) has shown that there are a number of problems associated with the standard technique developed by Aitchison (1986.141) to overcome this situation. This consists of a mathematical transformation conducted on the data which then allows the use of normal principal component analysis (PCA). The problem identified by Baxter with reference to archaeological material is that the PCA of such transformed data can be dominated by small subsets of minor or trace elements and can give rise to results with no substantive meaning and/or ignore much of the information in the data (Baxter 1992). Baxter goes on to suggest a way around this by dividing the data up into major and minor elements and then conducting PCA on both. The major set being subjected to Aitchisons transformation, the minor remaining un-transformed (or log-transformed). The results of these separate PCA's are then synthesised using Multiple correspondence analysis (MCA) of the correlation matrix. However, in a recent paper Tangri and Wright (1993) go further in their criti. ism of Aitchison's approach,

> "We therefore conclude the Aitchison's loglinear transformation is a dangerous attempt to correct the demerits of standard PCA. It tends to add spurious structure to the table of data, thereby producing distorted results. Users may therefore be better advised to put up with whatever distortions are inherent in standard PCA." (111)

This damning critique was answered by Baxter in the same issue saying that, although obviously not without its drawbacks, Aitchison's approach is a potentially useful tool (Baxter 1993.115). He goes on to say that while it may produce useful insights into data, he would not use it as the sole method of analysis. No doubt this debate will continue for some time to come.

Luckily, all the arguments concerning the validity of standard multi-variate techniques against the use of Aitchison's 'log-linear' transformation can be neatly side-stepped by simply making the data no longer 'constrained' or 'compositional' in the statistical sense (Baxter 1992.269). With the analytical data generated by this project this was done by removing the copper values from the data set. By doing this we are leaving data which now only sums to between 5% and 10%. This method is convenient in allowing standard multi-variate techniques to be used without criticism. However, it must be pointed out that compositions which contain several components with values of over 1.5% - 2%, or to put it another way, where more than one or two elements account for over 95% of a composition, the data must be treated as statistically 'compositional' (Baxter1992.269).

Despite the nature of our data allowing circumvention of the closure problem, the fact that we have one element which is present in significantly greater amounts than the others could also introduce spurious structure. In order to remove this problem, as well as to satisfy assumptions about the normality of the distribution and to stabilize the variability, it was decided to log-transform the data.

The fact that some of the trace element values were below the estimated detection limits means that the zero values are not true zero s but somevalue below the detection limit. In order to allow these values to be log-transformed a value of half the estimated detection limit was ascribed in these cases. This method is similar to that suggested by M.Leese of the British Museum Research Labs (pers.comm). In all cases, unless specifically stated, the data are assumed to be normally distributed.

These preparatory steps were used on all the AAS data produced by this project. The only exception being discriminant analysis which performs its own transformation of the data, making the log-transformation unecessary.

The more recent literature dealing with comparable material, advocates Ward's method cluster analysis (Leese et al 1989,241;Gilmore 1981,99) and/or one of several applications of principal components analysis (PCA) (Baxter 1989,1991). Consequently these methods were used along with discriminant analysis and, initially, k-means cluster analysis.

All multivariate techniques treat the data as if it were plotted element by element (variable by variable) in n-dimensional space (n being the number of elements), the idea being to look for points clustering together within that space. The methods differ in the way that relationships between the points are detected and in the transformations to which the data are subjected. Ward's method of cluster analysis is "an agglomerative method in which items are successively combined with existing clusters according to the reduction in error sum of squares" (Leese.1981.26). In the k-means method, "...k points are chosen as initial cluster means, with items being added to clusters according to distance; the cluster means are subsequently updated." (Leese.1981.26).

Ward's method provides a good initial exploratory method to establish a random cluster attribution which may then be refined by using k-means cluster analysis. The k-means approach will improve the attribution of clusters by re-running the program a given number of times (10 is advocated for the program used here), or until no relocation of cases to clusters occurs. However, after running both Ward's method and k-means for the raw data and finding almost exact replication, it was decided that Ward's method alone should be sufficient in most cases.

Principal components analysis attempts to visually plot all the cases in two-dimensional space, and to look for groupings within the plot. To do this axes are established along which there is most variation in the data, and each case is then plotted in relation to these axes. The first axis is the first principal component (pc1), the second axis is the second principal component (pc2), and

so on, there being as many axes as variables. However, with this technique, the assumption is made that the greatest proportion of the variability is in the first two components. For a further discussion of the relative merits of both PCA and cluster analysis, see Baxter (1989). As a general conclusion it should be stressed that no single method produces the 'correct' results. The approach adopted here has been to employ a selection of carefully chosen techniques by which to investigate structure within the data.

Where archaeological criteria exist which already serve to group the data by virtue of style or mint signatures, it has been possible to see whether these groups are reflected in the compositions. This has been done using discriminant analysis. Pioneering work was conducted by Carter and Frurip (1985) on the results of XRF analyses of Roman copper coins (Quadrantes) (see chapter one) with very good results. A more recent article by Carter (1993) applies the same methodology to the XRF analyses of a different category of copper coin (the As) by using the statistical program SPSS-PC with very good results. The same program was employed in the discriminant analyses used in this project. This has the advantage of allowing the direct importation of data in a spreadsheet format, as well as having very flexible and comprehensive reporting options. This is important because of the ability of discriminant analysis to attribute the groupings to specific elements or combinations of elements, as well as to supply a confidence interval for the attribution of a specific compositional set to a given group.

Discriminant analysis defines both the differences that exist between the groups and the variables that are responsible for the groups. To do this the program calculates what is termed a group centroid for each defined group. This is the point defined by the means of each group on each discriminant axis. The distance within the multi-dimensional space between these group centroids is termed the Mahalanobis distance. If the Mahalanobis distance between the centroids of two groups is relatively small, the two groups are defined as 'similar', if this distance is large then the groups are 'dissimilar'. By the same method the degree of likelihood that a given coin belongs to a specific group is also calculated, and the results of both can then be expressed as a probability.

2.4 Experiments in analytical precision and the established methods.

The accuracy and precision of the results reported in this thesis is obviously crucial to the success of the assertions made above. It is therefore important that it is demonstrated than the differences regarded as significant in the forthcoming case studies are real and not the result of experimental and/or sampling error.

As stated above the accuracy of the individual analyses was continually monitored by the use of standard reference materials. Agreement between the published compositions and those achieved by the author were very good to excellent, dependant on element. For example, the published zinc content for one SRM used is 0.28%, the values achieved by AAS ranged from 0.288% to 0.294%. Another SRM used has the published value of 0.037%, the achieved values are 0.036% and 0.037%. Nickel values varied between 0.689% and 0.710%, where the published value is 0.70%. Silver values (using prepared standards) gave between 3.98 ppm and 4.02 ppm on a 4.00 ppm standard. This would correspond to an equivalent silver percentage of between 0.667% and 0.670% at the dilution factor commonly used.

Reproducibility of results between different runs of analyses on both the same and different sample solutions was also tested. T-tests were then conducted on the data sets (assuming equal variance) to assess the similarities. Exceedingly good reproducibility was achieved between two sets of analyses conducted on the same sample solutions, with the likelihood of similarity being assessed at over 95%. The agreement between the results of analyses of different solution prepared from the same drillings was predictably less impressive. Nevertheless, a 93% likelihood of similarity between two separate solutions was calculated for zinc contents over 28 separate samples.

The degree of variation between drillings taken from separate locations on the same coin was also tested. The first test involved three drillings taken from one of the Fenny Stratford coin-blanks. These were analysed in the usual fashion and the results plotted together with the original analysis of an amalgamated sample taken from four locations. The resultant plot (Fig.5) clearly demonstrates that agreement is good, but that variation does exist. This is certainly what should be expected from the work of Sano and Tominaga (1982), and demonstrates the practicality of Charles' assertion that,

> "Where high levels of accuracy are required in analysis, multi-position sampling is an essential feature for metal objects" (1973.114)

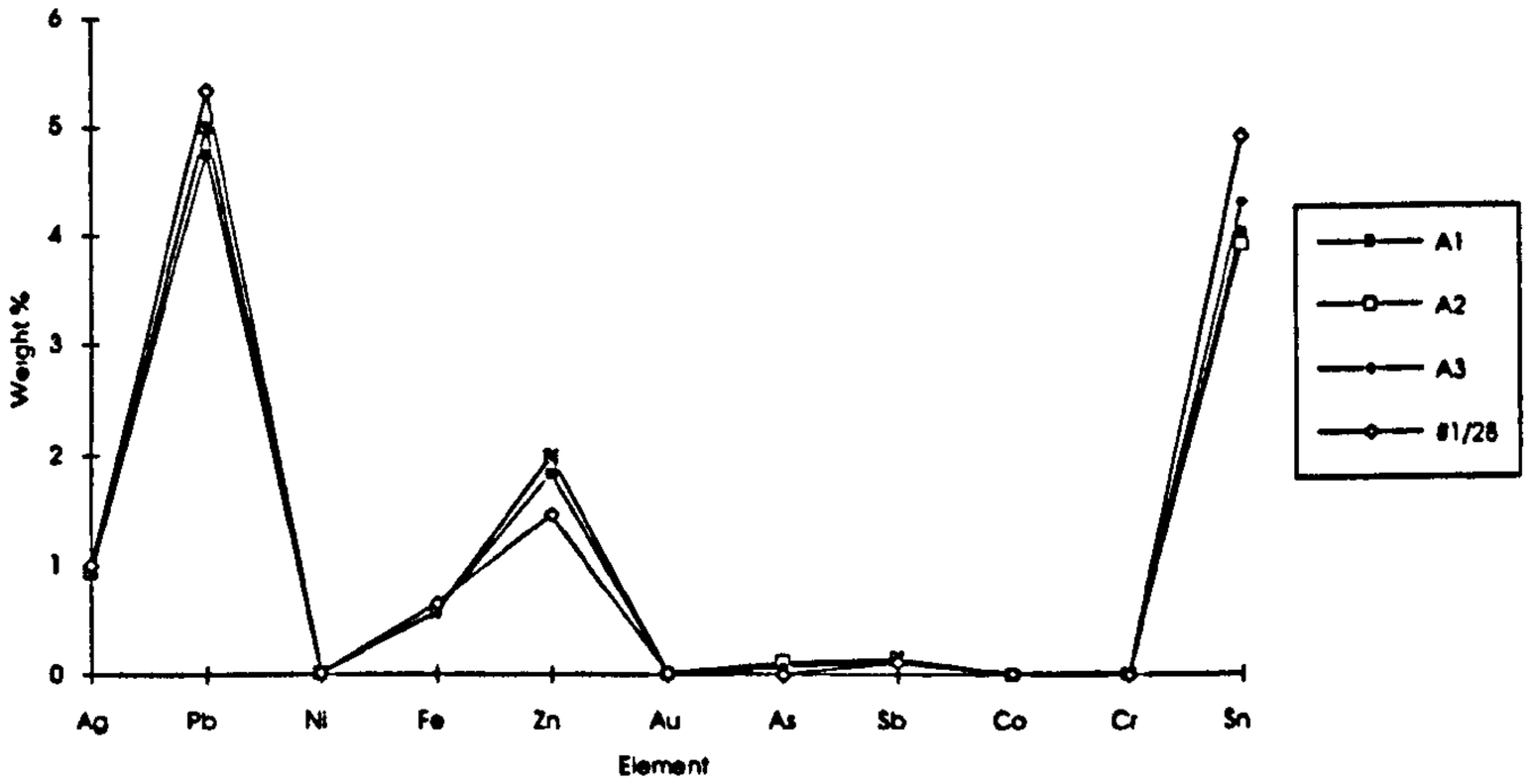


FIG.5. MULTIPLE ANALYSES OF FENNY STRATFORD COIN-BLANK NO.28.

If the aim of an analysis is to merely gain a general idea of a coins composition then a single sample may well be adequate. But if the aim is to gain a more representative analysis then a homogenised multiple point sample is the only satisfactory method. The 0.5% or so variability in the tin. zinc and lead contents shown in Fig.3 might well prove significant in any study of comparative compositions.

Another test took three drillings from one half of a coin and three from the other. The coin was a reduced Follis of Crispus, and was in very good, clean, and relatively un-corroded condition (Plate 1). The results (Table 3) further demonstrate the problems caused by segregation of the lead and tin if the location of the drill holes are not equidistantly placed. However, the excellent agreement between minor and trace constituents demonstrates that, at low levels, these components are adequately distributed to allow a representative analysis by this method. It is notable that even an element of negligible solid solubility, such as the iron, is distributed evenly enough to allow passable agreement to be achieved.

	Pb	Sn	Zn	Ag	Fe	Ni	As	Sb	Au
Top	15.90	2.712	0.069	0.611	0.470	0.035	0.293	0.116	0.033
Bottom	14.89	3.010	0.072	0.558	0.487	0.035	0.288	0.116	0.034

TABLE 3. DRILLINGS FROM OPPOSITE SIDES OF THE SAME COIN (WT.%).

Previous researchers have obviously been aware of the phenomena discussed in this chapter, and have, in a number of ways, tried to overcome the worst of their effects. We have already seen how Carters' work (1964, 1967, 1983, 1984 and 1986) established a pre-analysis cleaning and abrasion technique to allow reproducible XRF analyses of 'pure' copper and cementation-brass coins. This was an important development, but, as discussed above, has been inappropriately applied to more problematic copper-alloys since (Ziegler 1983, for example).

Cope (1974) was aware of the potential problems caused by both segregation and corrosion, although he mainly concentrates on the effects of corrosion. His assertion that,

> "Numismatists have been rather slow to discover the profound effects which corroded and other surface material included in the sample can have on the results of coin analyses..." (1974.71)

is followed by a resumé of work specific to this problem. It is quickly apparent that most of the work conducted up to 1974 was concerned with the problem as it affects silver coinage. The work of Carter is mentioned, but was in its infancy at the time and concerned with corrosion in relation to XRF analyses only. Consequently Cope was breaking new ground in suggesting that in alloys which contain metals of varying 'nobility' (varying electrode potentials) in separate phases then the metal of lowest 'nobility' will be corroded away preferentially (1974.72). He is

primarily concerned with the major components such as lead, tin and zinc, and is careful to point out that the degree of corrosion is also dictated by the nature of the environment.

To overcome these problems Cope advocates the removal of the corrosion layer by mechanical means (1974.74), followed by the gravimetric analysis of a complete half coin. Where the coins are liable to be corroded to some depth, such as;

> "...the later antoninianii (radiates) of the sole reign of Gallienus and almost all the late fourth-century small leaded-bronzes" (1974.75)

he recommends a process of 'fusion-reduction'. This method again takes a mechanically cleaned half-coin which is then rapidly melted in a graphite or alumina capsule. This is done at 1150°C, in the presence of carbon and hydrogen, the effect of which is to free the metal from any entrapped corrosion products, reducing some to the original metal (1974.76). This process, according to its author, produces a button of metal for analysis in which the majority of the metallic constituents have been recovered "in their correct proportions", and that any "siliceous or aluminous earthy matter" has been removed as an "insoluble powdery deposit which is easily removed..." (1974.75).

This is undoubtedly a highly accurate method for obtaining an analysis of the coin in its current form. It fails, however, to account for the migration of metal ions both into and out of the matrix. It is demonstrated in this thesis that iron can migrate into the voids within a coins metal matrix (see chapter 3), and the amount of copper picked up within the inside layers of vessels in which coin hoards have lain for 1500 years suggests that the reverse is also occurring (chapter 4). Furthermore, the extremely destructive nature of the method makes the analysis of suitable sample sizes impossible. Modern instrumental techniques detect both the atomic and ionic states of elements, making such extreme corrective methods unnecessary. The analysis by modern instrumental AAS of a small sample taken from multiple internal locations remains one of the most accurate ways of obtaining an analysis representative of the coins original composition.

The employment of Neutron Activation techniques has also been seen as a highly sensitive and non-destructive method of analysing severely segregated coins (Ravetz 1963, Gordus 1972, Gilmore 1981). However, as the whole coin is analysed, the corrosion altered surface zone is included in the overall analysis. This introduces an error which will produce a homogenised analysis of the coins composition as it is today and not of the original composition. Furthermore, the nature of the technique does not allow analysis of lead. The inclusion of the surface silvered layers, as well as the naturally enriched zone, also leads to erroneous results (chapter 4).

Chapter 3:
Case Studies

" Tace, sis, faber, qui cudere
Plumbeos numos soles!"

"You leaden coin-smith, do be quiet!"
Plautus, Mostellaria, 892

3.1 Barbar ous Radiates: The Fenny Stratford Hoard and the Walbottle Hoard.

3.1.1 General Introduction.

The investigation of these two groups was designed to address a number of numismatic problems. Firstly, a detailed study of the Fenny Stratford material was aimed at gaining an understanding of the different types represented in the hoard and to what extent they are related. This would also be the first comprehensive archaeometallurgical investigation of this type of material, and is consequently the most detailed case study presented here. An extensive set of rigorously conducted analyses which would, furthermore, provide a standard against which other, more piece-meal, data could be compared.

The compositional analysis of material from the Walbottle hoard acted as a direct comparison for the composition of the official coins in circulation at about the same time. This hoard also contained four coins which were identified by the numismatist as 'barbar ous radiates', these were also analysed. Comparison of struck 'barbar ous radiates' with the un-struck 'raw material' from Fenny Stratford is of interest, as well as looking for compositional confirmation of the official issues.

A further aspect of considerable interest became apparent during the preliminary evaluation of the AAS data from the Walbottle coins. This was when comparisons were made between these and other published analyses of numismatically identical coins (same issues, mints and catalogue attributions). This aspect of the analyses will be considered in chapter four.

In both cases note was made of the degree of corrosion affecting the coins analysed, none of which could be regarded as severe. Any compositional trait which could be ascribed to a post-depositional factor was noted.

3.1.2 The Fenny Stratford 'forgers' Hoard.

3.1.2.1 Introduction

Towards the end of summer 1990, during the course of roadworks at Galley Lane, Fenny Stratford (Roman Magiovinium), just south of Milton Keynes, a local metal 'detectorist' discovered what appeared to be the 'raw materials' for the production of unofficial Roman coins. The find comprised of three ceramic vessels containing three groups of material (Plate 2) and a pair of iron dies for striking the coins.

The discovery of such material, although not quite unique, is certainly very rare and, indeed, these are the first iron dies found in Britain. Coin blanks and pellets have occurred in association with struck unofficial coins, such as those in the Sprotbrough hoard (Mattingly and Dolby,1982) and the hoard from North Leigh Villa (Knight 1984). However, no struck coins were found in association with the Fenny Stratford material. Consequently the only reliable avenue for dating lay with the identification of the ceramic containers, although the size and weight of the blanks suggested a late third century date.

The identification of the pottery was carried out by P.T Marney of the Milton Keynes Archaeological Unit. Unfortunately the vessels proved rather unusual, although both form and fabric fall within a wide range of dates. Marney concludes that the vessels are,

> "poor imitations of the BB1 miniature cooking pot..."

and goes on to say that,

> ".....(the) vessels are not easy to date. Certainly a date of late second to fourth century AD would cover all possibilities, but is rather too generous. However, the use of 'wild arcs' as decoration, combined with the slenderness of the vessels, may perhaps indicate a date in the late third or early fourth century AD." (Marney,1990,unpublished pottery report).

This, of course, agrees with the date suggested by the size and weight of the blanks and pre-blanks, and, as shall be demonstrated later, is in agreement with the interpretation of the compositional analyses.

Within each of the three vessels was a distinct group of material. One vessel contained 352 blanks, another 246 pre-blanks (partly hammered flans) and the last vessel contained some 1250 cut lengths of cast copper-alloy rod as well as a small number of waste off-cuts and swarf.

Metrical analyses of the blanks and pre-blanks suggest a degree of control had been exercised over the size and weight of the flans. The average weight of 2.47gm is in close agreement with what one would expect for official late third century base antoninianii ('radiates') as is the range of flan sizes (12-21mm).

3.1.2.2 Sampling and Analysis.

In sampling the hoard, each group of material was treated as a separate population in isolation. The aim of the study was to characterise each group, and to investigate any variation in composition that may occur within a group. It was decided to randomly select ten pieces from each of the groups, using accepted sampling theory (see chapter 2), with a further five pieces being selected to illustrate the varying degrees of corrosion present.

An initial viewing of the data quickly established that there were two very distinct groups of material, corresponding to the blanks and pre-blanks on the one hand, and the lengths of cut rod on the other. The blanks were distinguished by a significant zinc content, and the lengths of rod were notable for their relatively high tin content (fig.6).

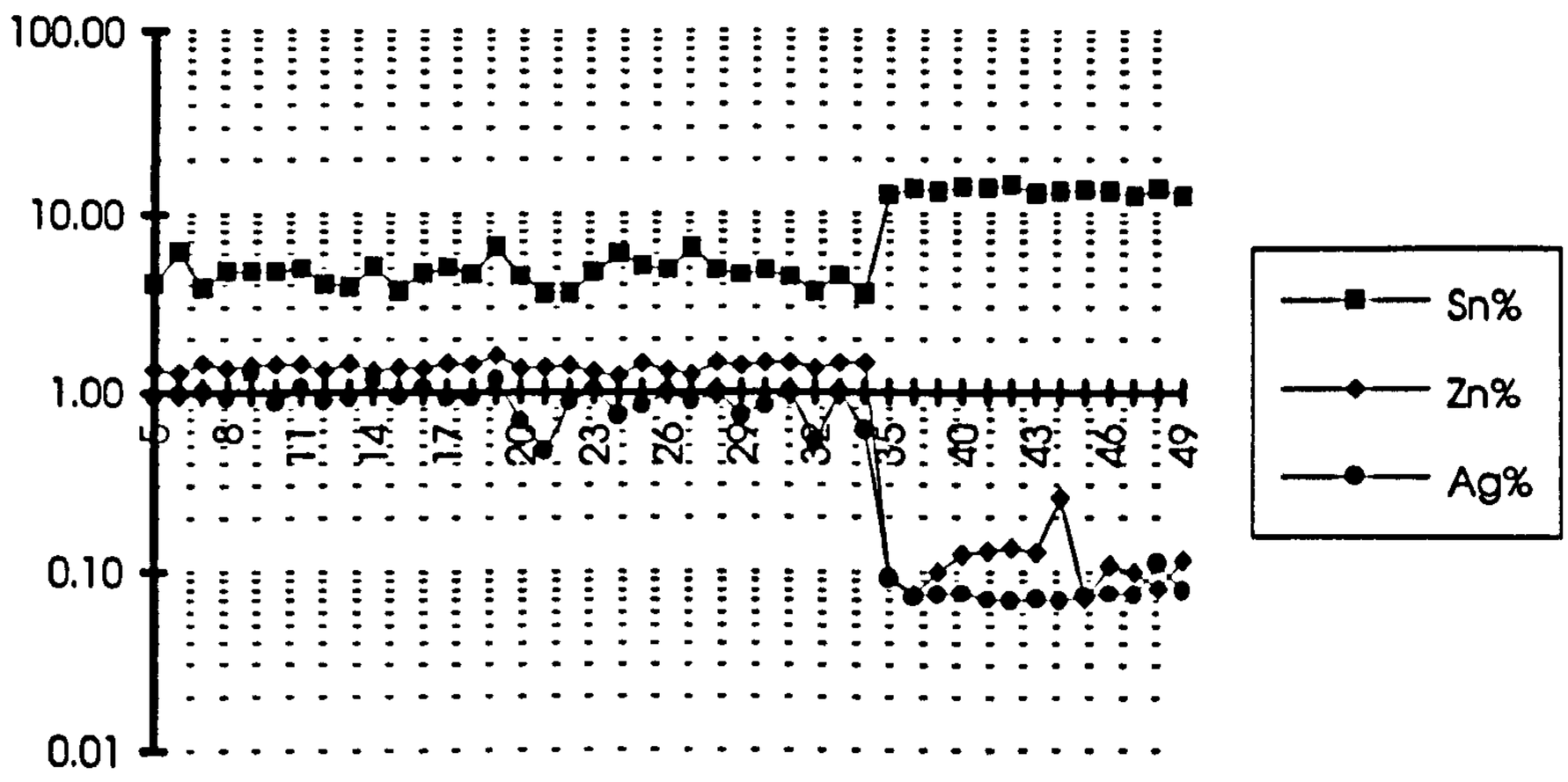
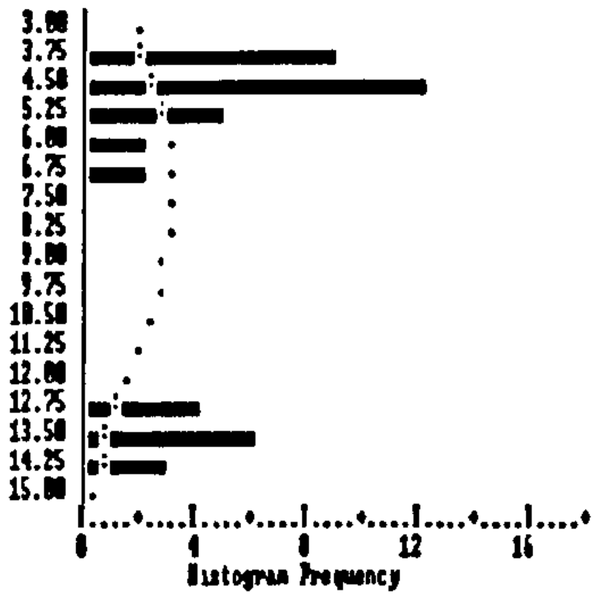


FIG.6. PLOT OF RELATIVE SILVER, ZINC AND TIN CONCENTRATIONS.

BLANKS AND PRE-BLANKS ARE NOS.5-33.

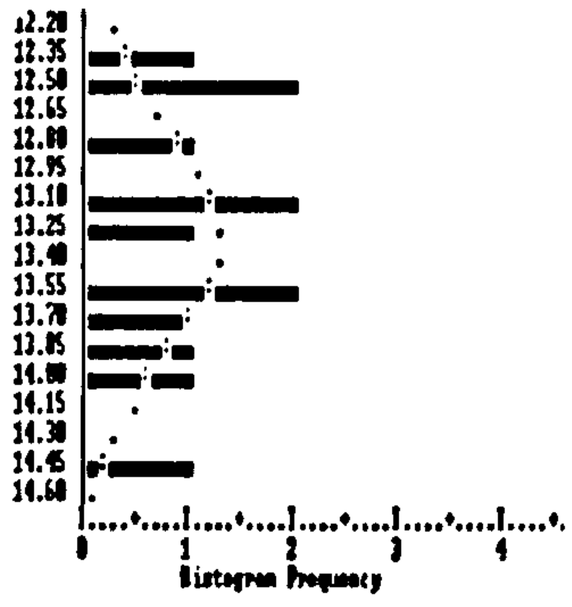
PELLETS ARE NOS. 34-49.

Initial statistical examination of the complete data set suggested that not all the elements conformed to a normal distribution (fig.7). However, this was shown to be the result of having two normal distributions present, representing the 'pellets' and 'blanks' respectively. When the lengths of cut rod ('pellets') were separated from the blanks a semblance of normality returned (fig.8). It was therefore decided to separate the data, and to treat the 'pellets' and 'blanks' as discrete groups.



(fig.7)

Tin percentage frequency for all data



(fig.8)

Tin percentage frequency for 'pellets'

The transformed data was then run through a clustering program using Wards method to confirm the primary analysis of two distinct groupings - 'pellets' and 'blanks' - this was, of course, confirmed (fig.9).

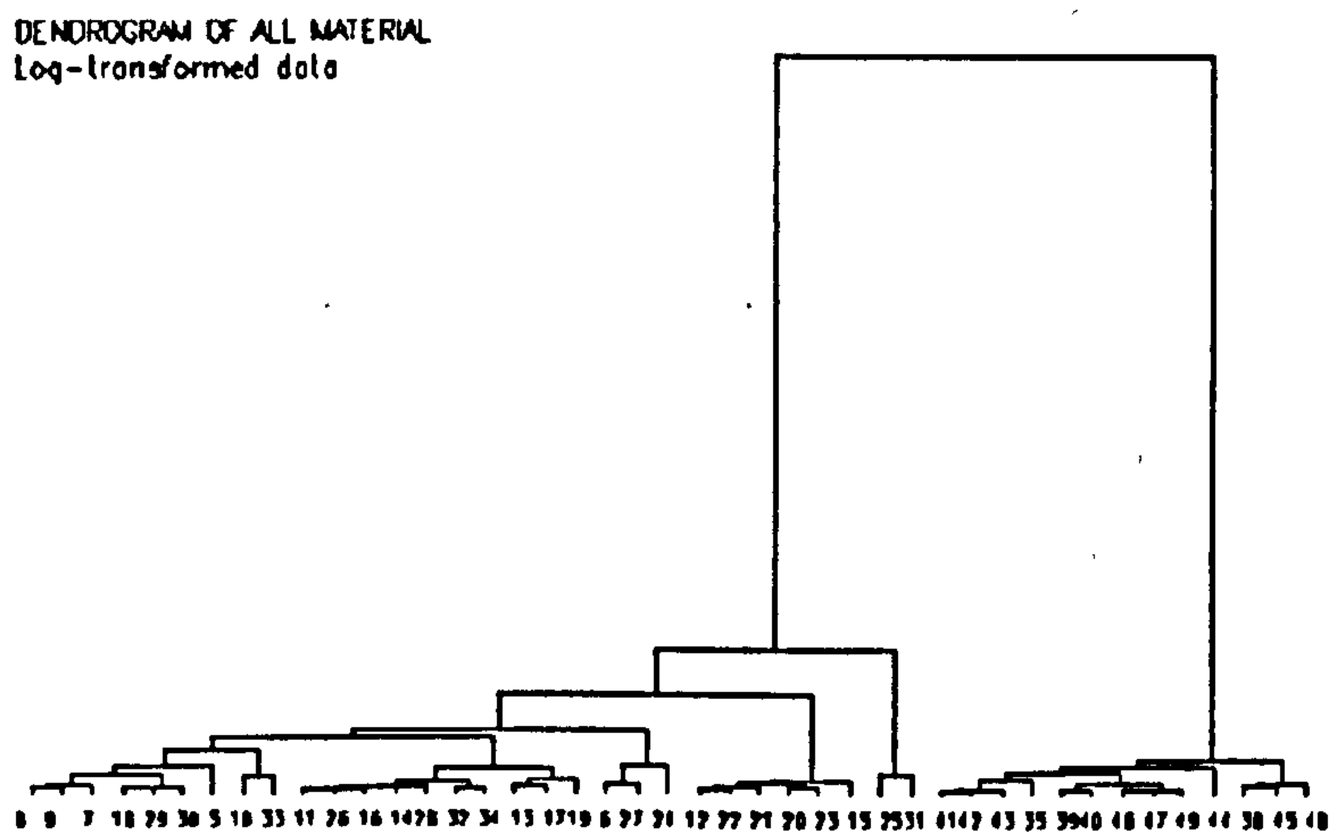


FIG.9. DENDROGRAM OF ALL DATA.

The same data was then subjected to PCA of its covariance matrix. This version of PCA is less affected by outliers and is usually regarded as statistically 'safer' than PCA of the correlation matrix (Shennan 1988.262). The results of this analysis agree with the groupings suggested above, and also highlights the separation of the two blanks with a markedly higher cobalt content (Nos.25 and 31).

The next stage was to divide the data into 'blanks' and 'pellets', and to re-run the analyses on each group.

The larger of the two groups, the 'blanks' and 'pre-blanks', consisted of thirty analyses. The Wards method dendrogram (fig.10) continued to separate out 25 and 31 as being significantly different to the rest. It also sub-divides the remaining twenty-eight samples into at least two other main groups.

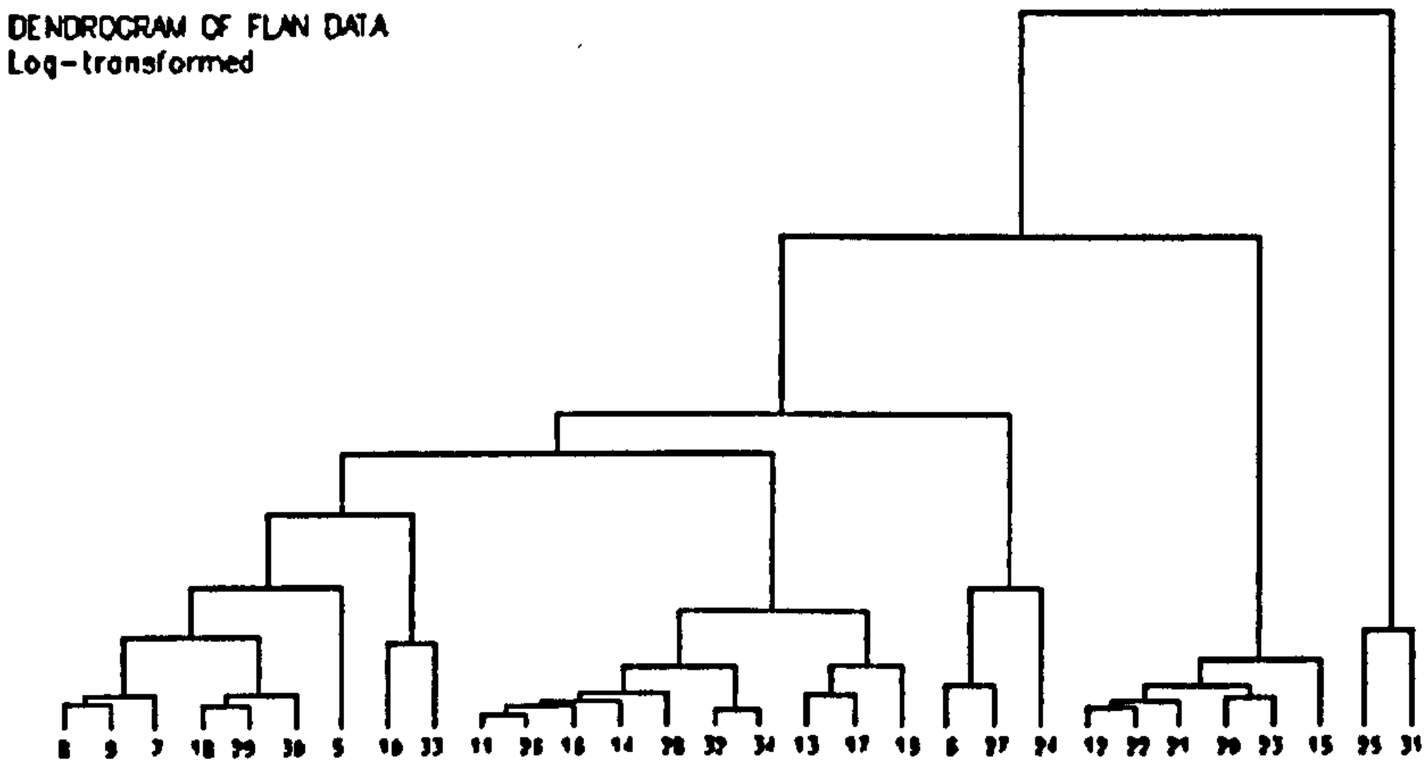


FIG.10. DENDROGRAM OF BLANKS DATA.

The PCA is largely in agreement, clarifying the situation by limiting the groupings to three, or, at most, four (fig.11). The group consisting of 25 and 31 is relatively very different and in many ways can be treated as an outlier. The remainder divide clearly in two, with the larger group being less discrete. There is, however, slight disagreement between the dendrogram and the PCA on the exact allocation of some group members. Sample 24 is undecided as to which group it belongs to, and it seems unlikely that any fourth group can be satisfactorily defined. It is, therefore, probably safer to say that, looking at all the elements analysed, the 'blanks' can be divided into two groups, with a further group of two samples being defined by their cobalt content.

The 'pellets' group consists of thirteen samples only. The Wards method dendrogram and the PCA (figs.12 and 13) are largely in agreement in suggesting four groups. The most different group (38, 45 and 48) seems to be characterised by relatively higher lead and iron. The second most different group, that consisting of No.44 only is marked by a higher iron content, whereas the remainder appear to differ only slightly in composition.

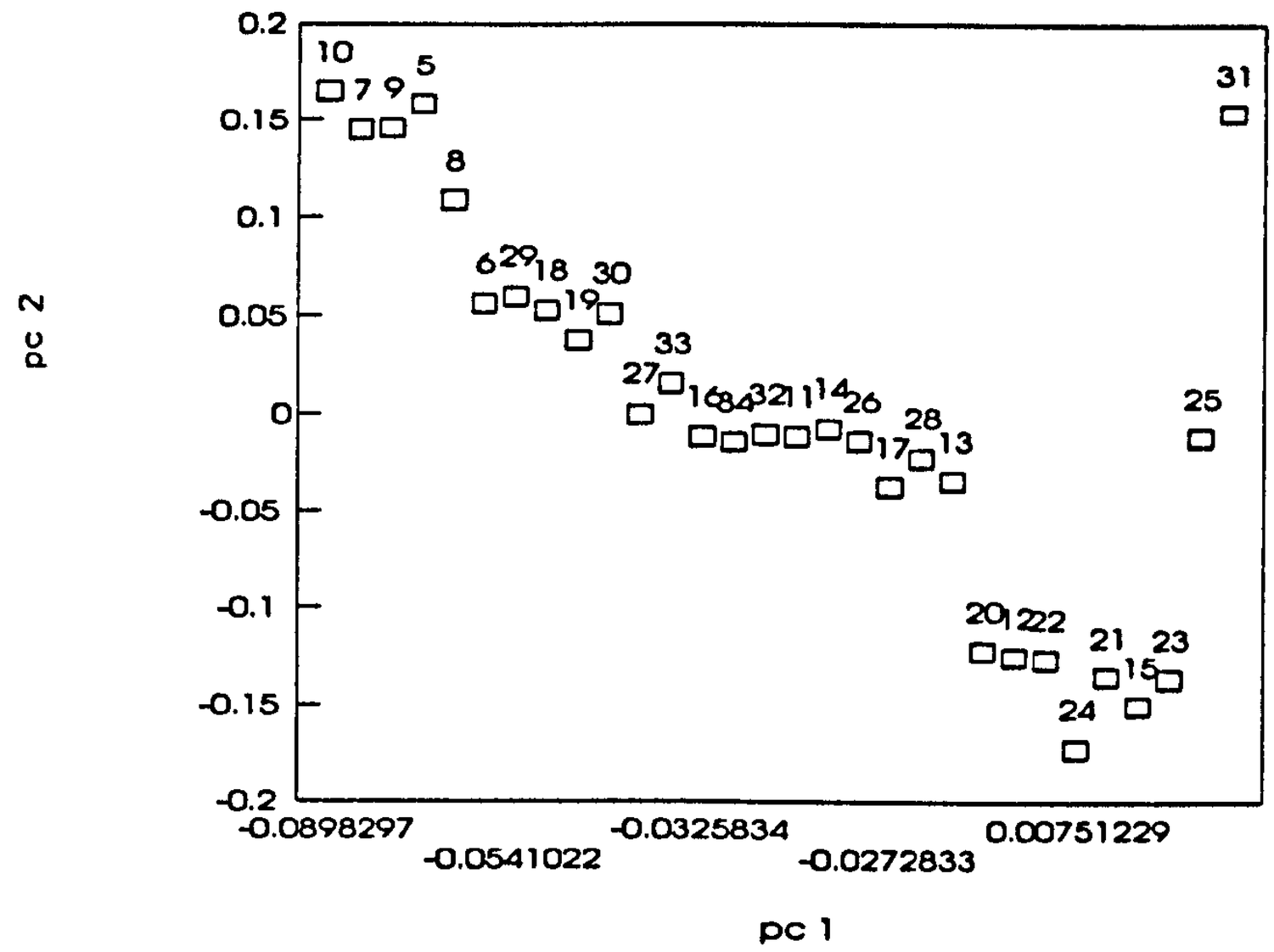


FIG.11. PCA OF ALL BLANKS.

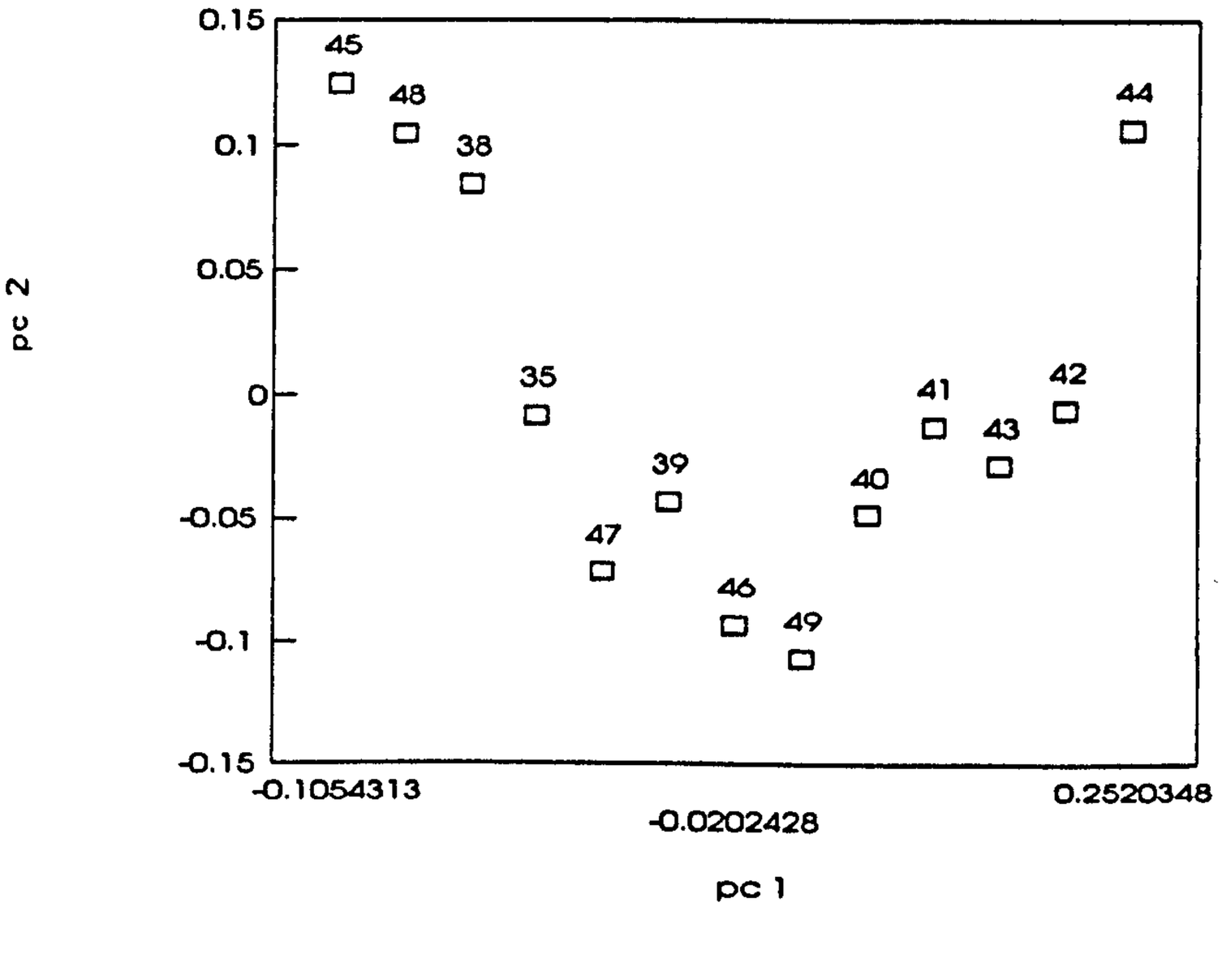


FIG.13. PCA OF PELLET DATA.

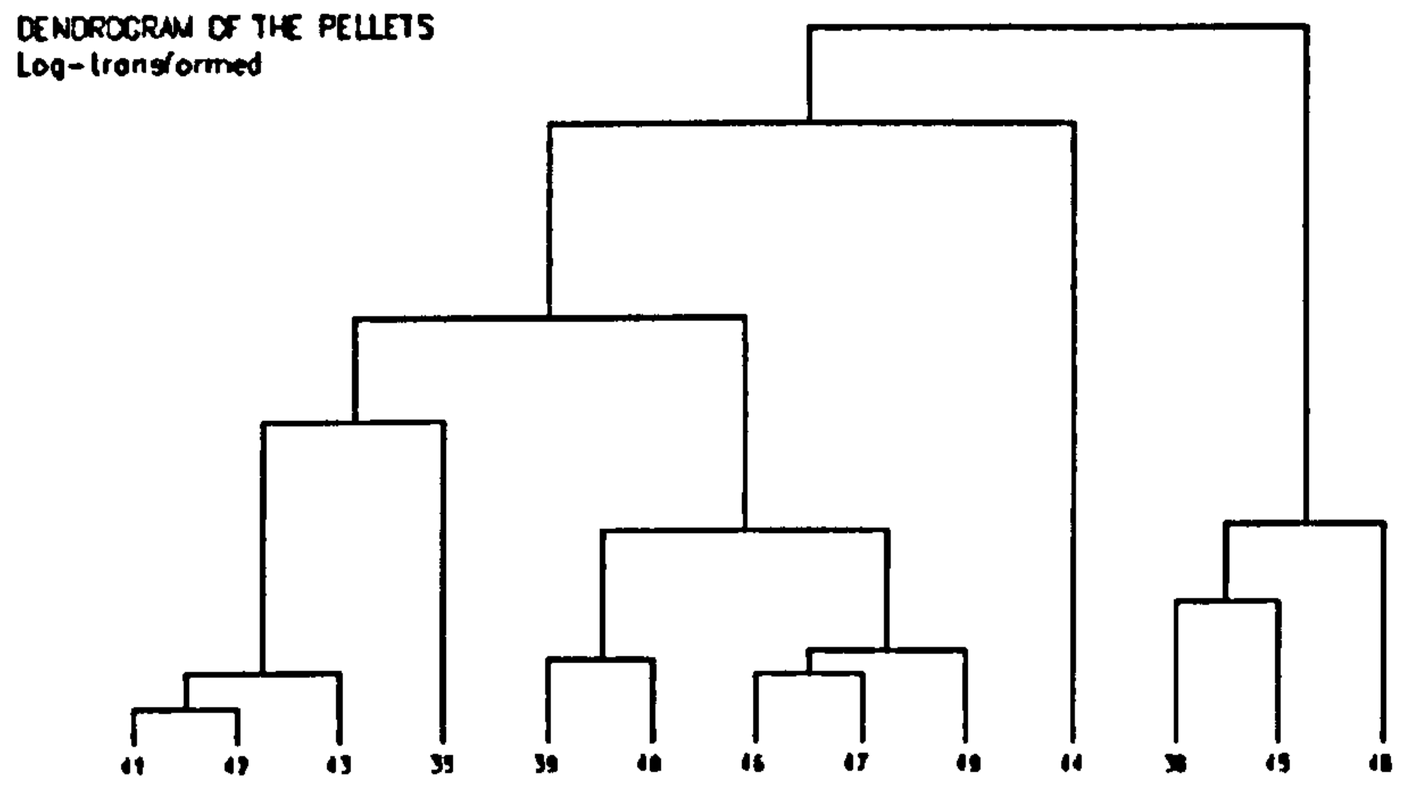


FIG.12. DENDROGRAM OF ALL PELLET DATA.

If we return to the archaeometallurgy for a moment we can suggest a further division of the data. Based on the assumption that certain metallic constituents would have been measured and controlled in antiquity we can separate the 'alloying components' from those elements which are the result of the smelting technology (impurities from the ores or fluxes). The tin, zinc, silver and lead can therefore be regarded as 'controlled' components, whereas the nickel, iron, arsenic, antimony and cobalt would not have been detectable in antiquity and must be regarded as 'impurities'. We can, therefore, expect different groupings for those elements present as impurities and those elements which relate to an alloying process, whether as a carry-over in scrap, or directly.

To investigate this the data were again sub-divided, this time into 'major' and 'minor' components. The 'blanks', although showing three clear clusters in the dendrogram of 'major' components, failed to reproduce this in PCA (figs.14 and 15). This suggests that the 'major' components are distributed fairly uniformly within the alloy, the variation picked up by Ward's method being insignificant and more likely to be a product of the technique rather than the material.

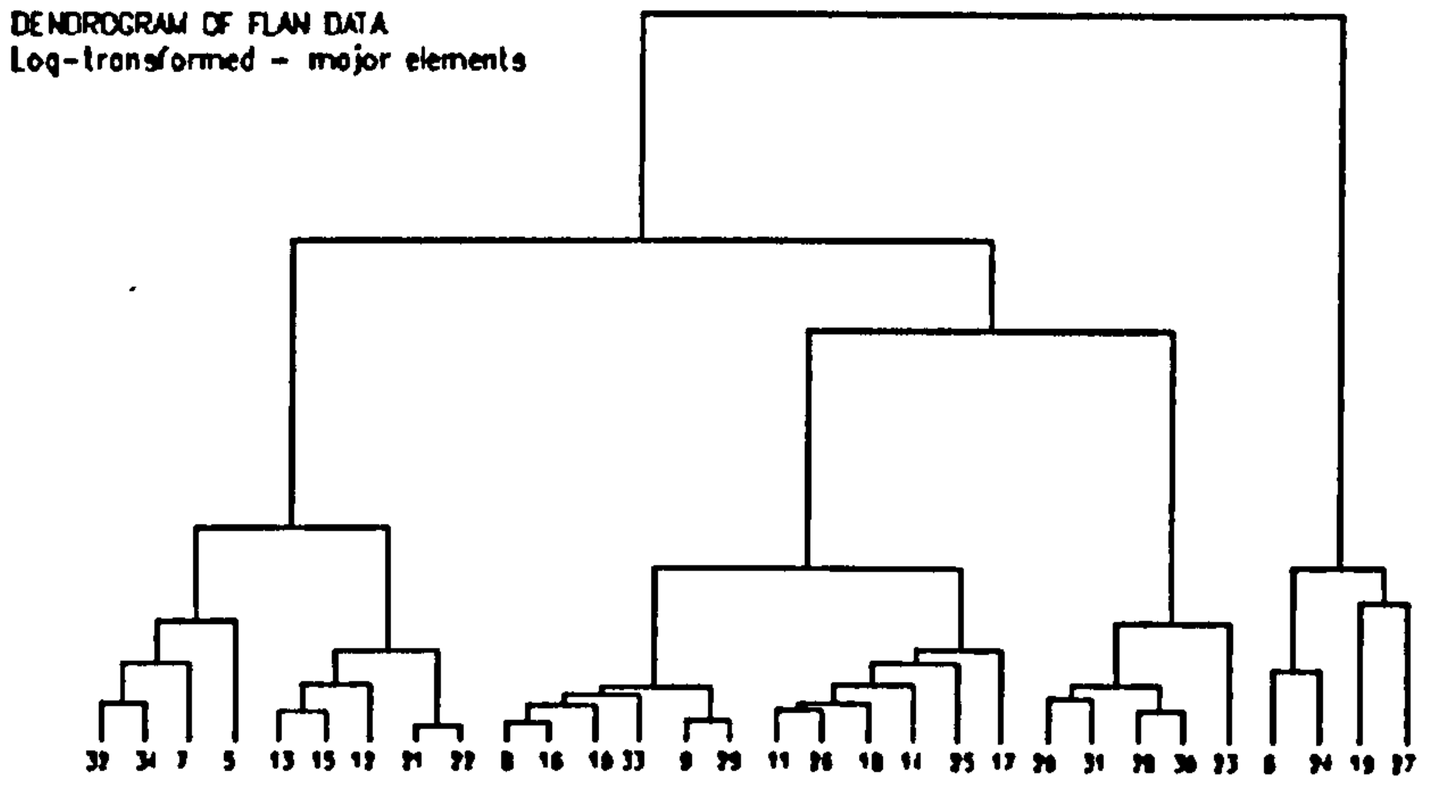


FIG.14. DENDROGRAM OF MAJOR ELEMENTS IN BLANKS.

The 'minor' constituent elements, however, show discrete clusters in both methods of analyses (figs.16 and 17). The samples containing significantly higher cobalt values (25 and 31) continue to comprise the most different group. Two further groups are apparent, and are well separated. The groups are similar to those suggested in the analysis of the 'blanks' by all elements (fig.11), and the clarification of the groupings by this separation is encouraging.

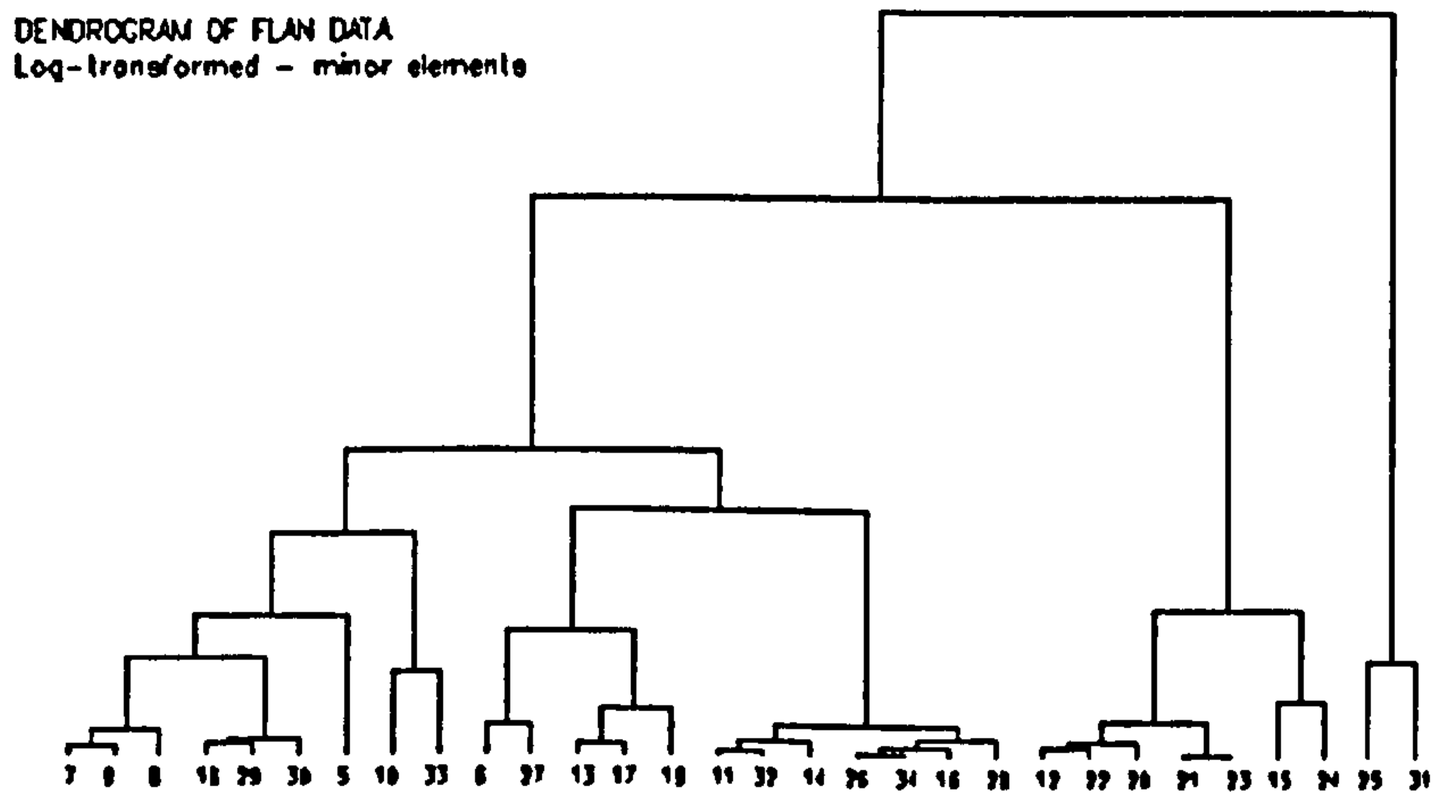


FIG.17. DENDROGRAM OF MINOR ELEMENTS IN BLANKS.

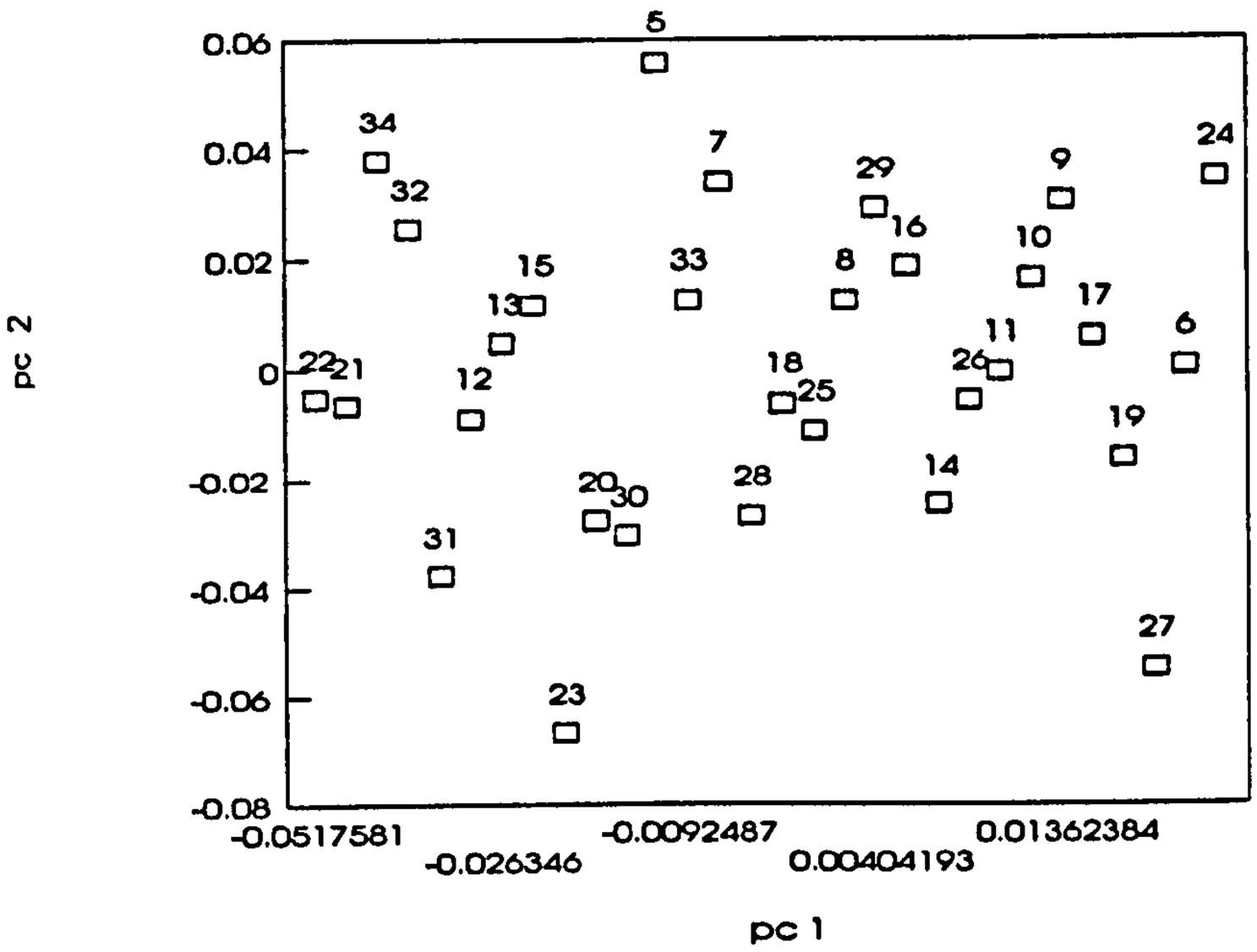


FIG.15. PCA OF MAJOR ELEMENTS IN BLANKS.

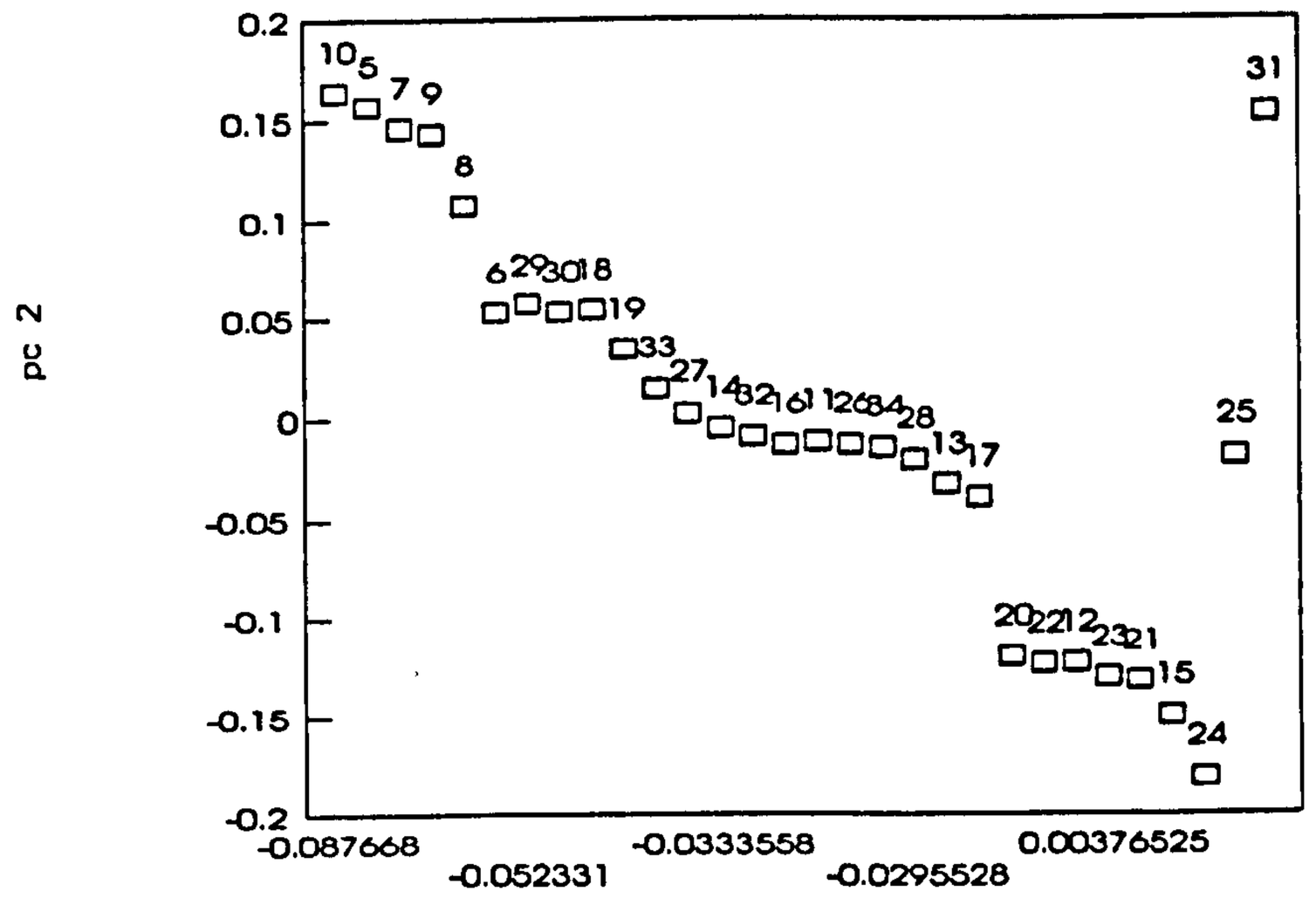


FIG.16. PCA OF MINOR ELEMENTS IN BLANKS.

It would certainly seem that the groupings within the 'blanks' data are primarily due to the 'minor' constituents.

The 'pellets' also show less structure when the clustering is based on the 'major' elements than when it is based on the 'minor' elements (figs.18 and 19). The Wards method dendrogram for the 'minor' elements (fig.20) clearly shows two groups, and this is supported by the PCA. Little reliable structure is evident from the 'major' elements, and the PCA is similarly diffuse.

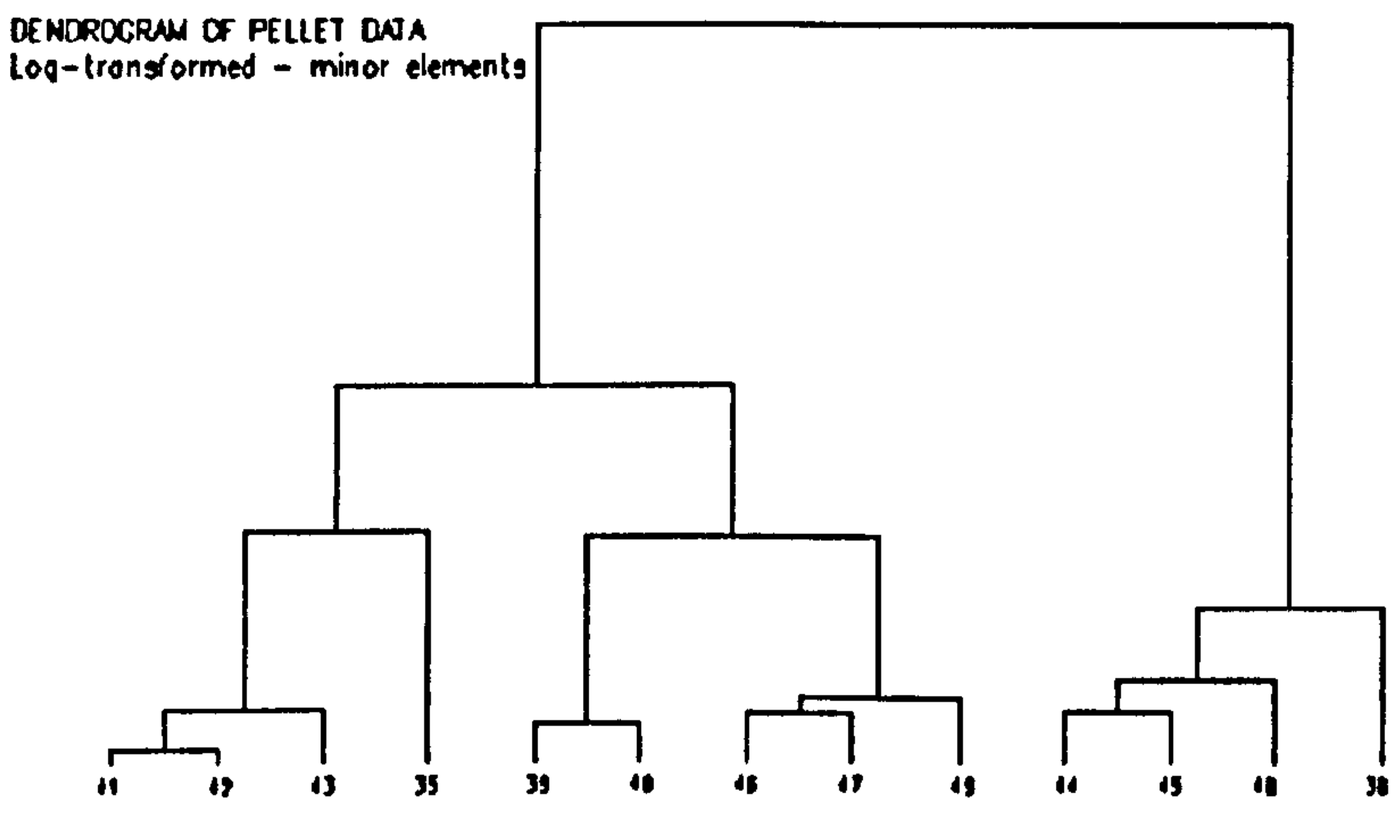


FIG.20. DENDROGRAM OF MINOR ELEMENTS IN PELLETS.

In order to check whether the compositional groupings encountered are significantly different or just artifacts of the clustering procedure, the data were submitted to discriminant analysis. This process calculates the relative probability of membership of each case to the specified group. The results confirmed the attributions in all cases with the probability of membership being less than 99% in only three cases. This is demonstrated in the table for the 'pellets' by minor components shown in Table.4

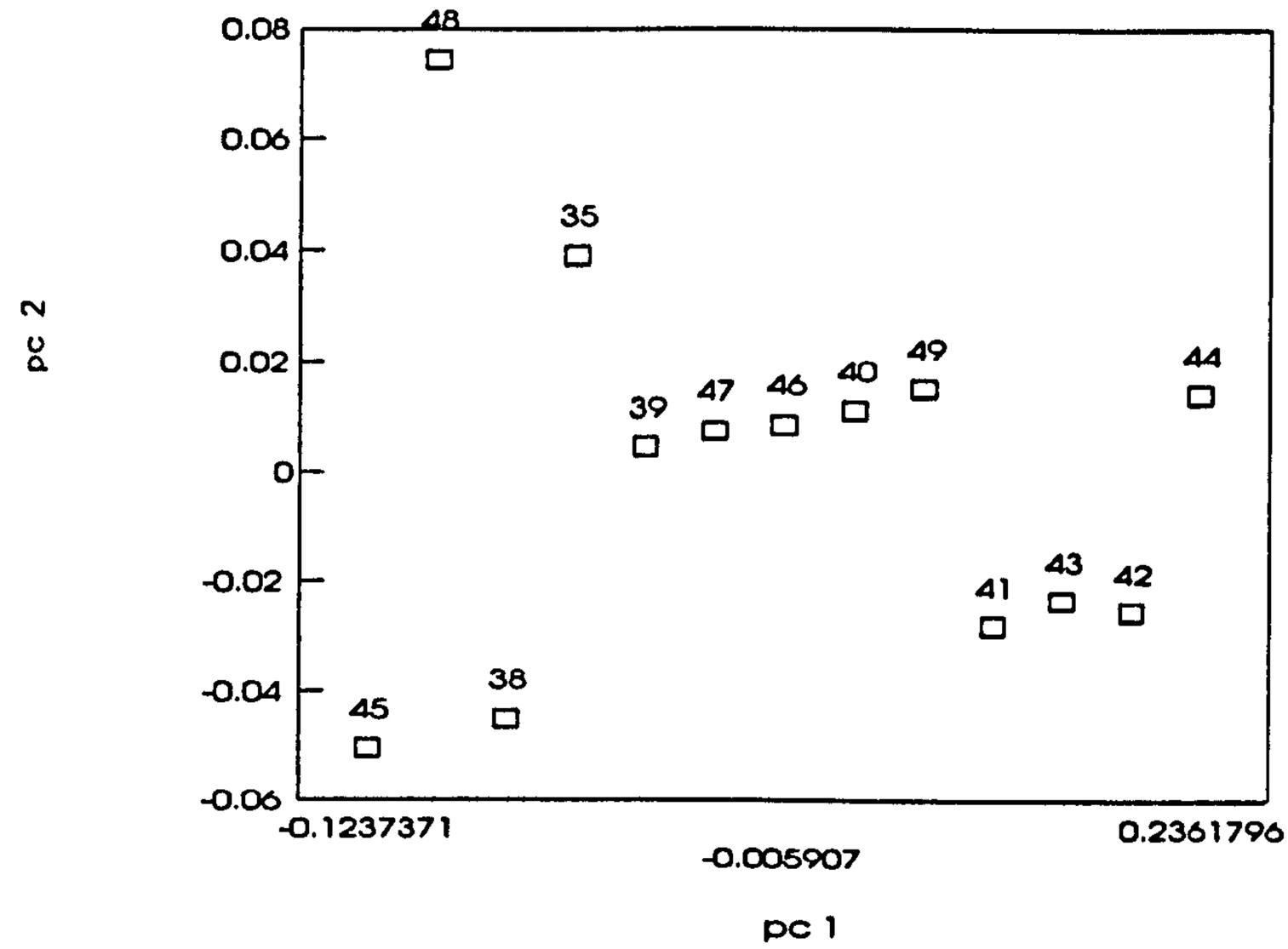


FIG.18. PCA OF MAJOR ELEMENTS IN PELLETS.

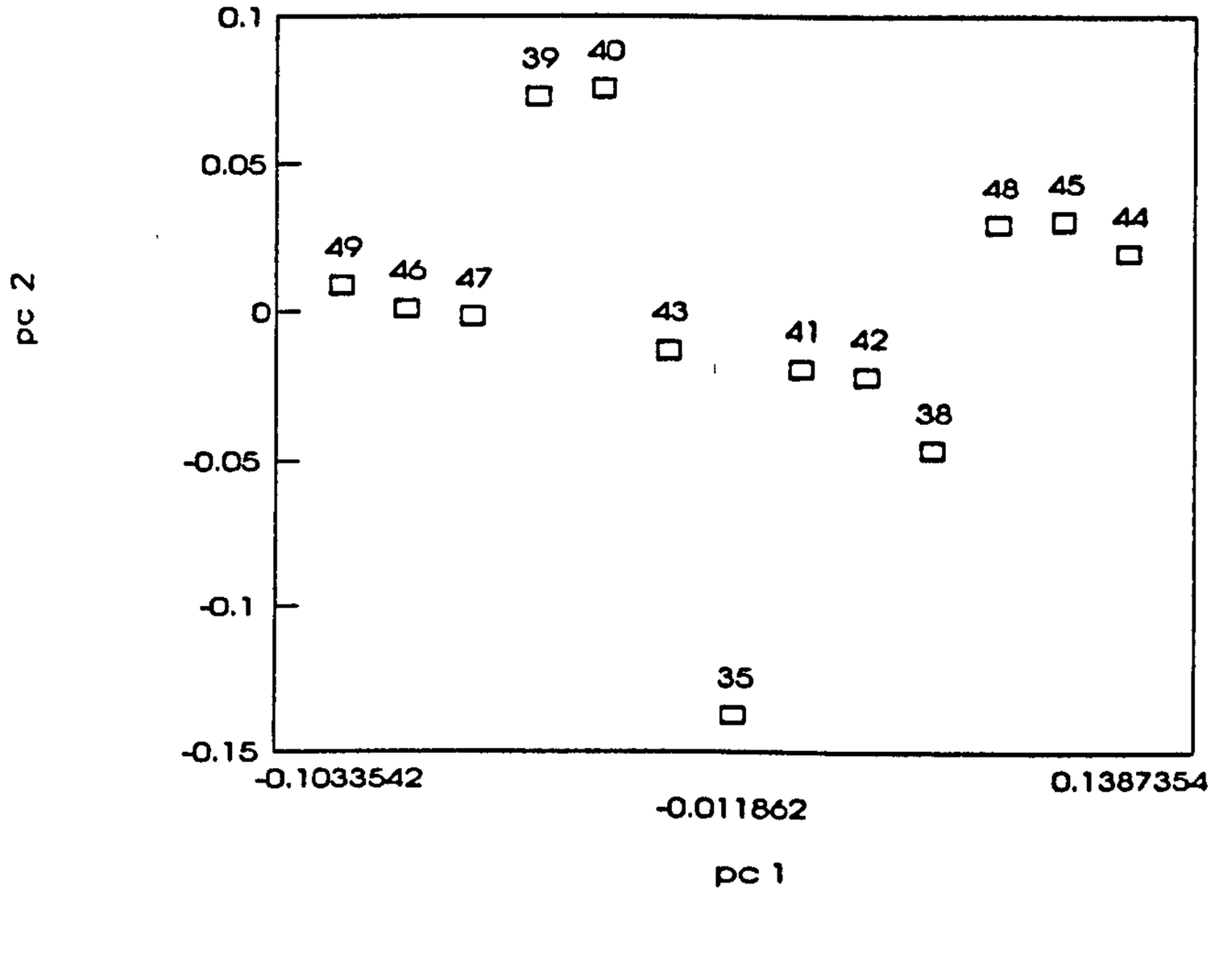


FIG.19. PCA OF MINOR ELEMENTS IN PELLETS.

SAMPLE	GROUP	Highest Group Probability	Second Highest Group Prob.
35	1	1.0000	.0000
38	3	1.0000	.0000
39	2	1.0000	.0000
40	2	0.9999	.0001
41	1	0.9997	.0003
42	1	1.0000	.0000
43	1	0.9986	.0014
44	3	1.0000	.0000
45	3	1.0000	.0000
46	2	1.0000	.0000
47	2	0.9997	.0003
48	3	1.0000	.0000
49	2	1.0000	.0000

TABLE. 4.

Discriminant analysis can also indicate which variables are responsible for the clustering. The 'major' ,or controlled, elements responsible for the slight variation picked up in the 'blanks' group are tin and lead (F values of 30.34 and 183.5 respectively). However, the real groupings, by the 'minor', uncontrolled, elements are defined by the cobalt and nickel contents (F values of 841.0 and 28.05 respectively). The groupings of the 'pellets' are similarly defined; lead is again responsible for the groupings based on the controlled elements together with zinc (F values 2.30 and 39.99 respectively), and the iron content is confirmed as being responsible for the 'minor' element groupings (F value of 87.10) .

3.1.2.3 Discussion of Analysis.

By using a combination of complimentary multivariate techniques it has been possible to discover sub-groupings of compositional types, to confirm the reliability of the groupings and to identify the elements responsible for those groupings.

The 'blanks' are grouped into three or four clusters when we consider all the elements together. However, the groups are more clearly defined once the 'major' and 'minor' elements are treated separately. Furthermore, it should not be surprising that the 'major' elements produce different and far less discrete groupings than the 'minor' elements. Indeed, it appears unlikely

that the 'major' elements are showing any clear separation other than that accountable by segregation, sampling error and experimental error. The fact that discriminant analysis tells us that what variation there is is due to the lead and tin values only supports this contention, given the likelihood of precipitation of these metals during the cooling of the alloy. This obviously suggests a relatively homogeneous distribution of the 'major' components throughout the group, which must also indicate the operation of certain standards in the production of the alloy across a number of possible batches of metal.

The 'minor' elements, on the other hand, give a far clearer division of the group into three clusters. The discriminant analysis gives cobalt and nickel as the responsible metals, both of which have been seen as being of use in archaeometallurgical studies elsewhere (Hauptmann 1989). Cobalt and nickel are usually impurities associated with copper, being used to link metallic copper with its likely ores. It is therefore probable that the groupings apparent within the 'blanks' reflect differing sources of copper, rather than any of the other 'major' constituents.

The 'pellets' are divisible into three main groups, and, as above, the only significant groups are characterised by the 'minor' elements. In this case it is the iron values which the discriminant analysis tells us are responsible for the groups. This may again be related to the source and smelting of the copper as iron oxide can be used as a flux. However, this may also relate to the burial environment, especially considering the two iron dies which were found alongside the group. Unfortunately, being a metal detector find, no record of the relative position of the groups to the dies exists, and so this hypothesis cannot be tested.

It was also possible to make some general assumptions about the relationships between certain of the elements from the principal component and discriminant analysis. Tin and lead appear closely related, as do silver and zinc. If ratios are calculated for each of these pairs it becomes apparent that, although, there are different ratios operating between the 'blanks' and 'pellets', as expected, within the groups these ratios are fairly consistent.

The lead-tin ratios have a mean value of 0.82 and a standard deviation of 0.1 for the 'blanks', and 1.7 (std 0.08) for the 'pellets'. These figures may suggest a ratio of tin to lead similar to that employed in the official coinage. Cope (1968) suggests the use of a preliminary 1:1 lead-tin alloy in the production of late third/early fourth century coins, and we may be seeing a similar practice at work here. If the Fenny Stratford 'blanks' alloy was partly produced from melted down official coins, we may be seeing a carry over of the official alloy ratios.

The silver-zinc ratios for the 'blanks' have a mean value of 1.6 (std 0.4) and 1.6 (std 0.7) for the 'pellets'. Again the consistency notable, and the fact that the ratios are the same for both

groups may suggest the existance of a value relationship between these two metals. This must further suggest that a considerable degree of control was in all likelihood exercised over these materials by the 'forger'. Both silver and brass (orichalcum) were valuable materials, even at the concentrations found here.

3.1.2.4 Physical examination.

Each of the samples analysed chemically were also subjected to a physical examination involving the use of optical microscopy. A selected example of each group was mounted in polyester resin and the exposed edge was ground and polished in preparation for metallographic examination. In order to show the crystal structure of the sections the metal was etched with either alcoholic ferric chloride or ammonium persulphate. The etchants were prepared according to Scott (1987.98-111). It was found that ammonium persulphate was a better etchant for the high tin alloy of the pellets, whereas ferric chloride was more suited to the purer copper of the blanks and pre-blanks.

In order to make the removal of the blank and pre-blanks from the resin possible, a method was devised whereby the resin block could be easily split along the line of the sample. The pellet was not to be reclaimed, however, and so it was decided to section it longitudinally, after first taking the 'top off' in order to examine the orientation of grain growth.

<u>The Blank (sample No.12):</u>

A cursory examination under a low powered microscope quickly established that this blank was produced from hammering together two of the pre-blanks. Examination of the remainder of the sample revealed that four others had been prepared in the same fashion (Nos.11,13,15 and 17).

Metallography showed small equi-axed grains of a single phase. Grain size is in the order of 20μm. A number of grains showed twinning, although by no means all, and several also exhibited strain lines (Plate 3). This suggests that the blank had been prepared by alternate annealing and cold-working. The presence of strain lines confirms a final hammering process.

There is also a fairly considerable degree of porosity in the alloy, however, there is virtually no intergranular corrosion, except for that at the very surface of the blank.

<u>The Pre-blank (sample Nos.25 and 27):</u>

These appear to be cast globules of copper-alloy which have been subjected to varying degrees of hammering. A preliminary examination revealed a number retaining a lip where the molten metal had overflowed the top of the mould (No.25, Plate 4), this supports the assertion that they

are virtually as cast. It is presumed that they would have been cast in open pottery moulds with individual depressions for each blank. This is a technique which has been documented for the coinage of the Late Pre-Roman Iron Age in this country (Tylecote 1986.114), but has not hitherto been found in a later context (see chapter 5 for discussion).

Metallography revealed slightly different structures depending upon the degree of cold-work. Both, however, were quite porous again, although no corrosion had penetrated beneath the surface of the pieces.

Both showed small cored dendrites radiating inwards from the edges of the blank, together with numerous cored grains with remnant dendritic structures (up to 30 μm) (Plate 5). Pre-blank No.25 also showed several grains with strain lines, indicating that a greater degree of cold-work followed the initial casting process than for No.27.

The Pellet (No.47) (Plate 6):

Examination under a low powered microscope revealed that the pellets had been cut from cast rods of alloy, probably by a cold-chisel. The photograph clearly shows the chisel cut penetrating one-third of the pellet, the remainder being broken by the force of the blow. Both ends of the pellet exhibit the same features. Similar evidence has come from North Leigh Roman Villa (Knight 1984.1)

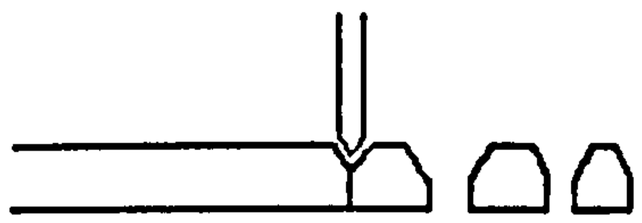


FIG.21. SUGGESTED METHOD OF PELLET PRODUCTION.

Metallographic examination of the sections prepared from the pellet revealed a fairly porous dendritic structure (some cored) consistent with the rod being cast (Plate 7). Again no corrosion had penetrated into the alloy matrix. Closer examination showed a two-phase system, with the α and δ-eutectoid defining the grain boundaries and infilling the arms of the dendrites. The existence of such a eutectoid is common in archaeological bronzes containing over 10% tin and tends to make the alloy brittle and difficult to work (Scott 1987.24). This brittleness would explain why the chisel cuts only penetrate slightly into the rod; the force of the blow being sufficient to shatter the brittle metal.

The majority of the dendrites appear to orientate inwards along their central axes, this is consistent for an alloy cooling quickly from the outside inwards as would be expected in this case.

Examination of the cut edges revealed distortion and strain lines consistent with the use of a cold-chisel.

3.1.2.5 Scanning electron microscopy and EDAX analysis.

One example from each of the three groups was prepared for analysis, being the same samples that were examined metallographically in the previous section. A number of samples were also subjected to a surface analysis only.

EDAX analysis of the metallographic polished sections produced results largely consistent with the AAS (appendix 3). Where this technique did supply additional information is in the detection of sulphur. This element is not detectable by AAS, and its detection by EDAX is of interest.

Copes' gravimetric analysis gives figures of between 0.02% and 0.6% for sulphur in Roman copper-alloy coins (Cope 1974.168), probably reflecting the smelting of some sulphide ores. The figure of 0.34% for the Fenny Stratford material is therefore in keeping with Copes' findings and must also reflect the origin of part of the metal.

Inclusions noted in the polished sections were also analysed. Most of these proved to be minute globules of a lead rich alloy (70%+), unsurprising given the insolubility of lead in copper. No sulphide inclusions were identified.

Analysis of the corroded surfaces of three blanks showed a relative increase in the iron and lead to copper ratios. Some iron would in all likelihood come from the surrounding environment (in the electrolyte), and possibly related to the dies. The lead on the otherhand must have come from the alloy itself. Calcium, silica and aluminium are also present (appendix 3) and must again be related to the surrounding environment, being common to most soils. All the elements are combined with a light element not detected by the analyser, which makes up some 60% of the corrosion products. This is presumably oxygen, hydrogen and/or carbon, suggesting that the corrosion products consist of oxides, carbonates and/or hydroxides. Chlorine is also present in very small amounts and must again be associated with the surrounding environment.

Blank No.5 has an iron content (determined by AAS) of 2.31%; considerably higher than any of the other samples. The blank is also covered with what appears to be iron corrosion products. This was confirmed by a surface analysis, showing 17.9% iron, the largest detected component (the bulk again being oxygen,carbon and/or hydrogen). This must relate to the position of the blank during burial, suggesting that it must have been close to the iron dies, or some other iron object. Whether the 2.31% iron detected in the bulk analysis is the result of contamination from

the surface during sampling, or whether it results from diffusion of iron into the alloy itself is still unclear. Certainly the metallography suggests that there can have been very little movement of electrolyte into the metal matrix, there being no intergranular corrosion or any great porosity. This would make contamination the more likely option and seems to indicate that, apart from surface effects, the internal composition of the Fenny Stratford material has been relatively unaltered by its burial environment.

3.1.3 The Walbottle Hoard.

3.1.3.1 Introduction.

The Walbottle hoard was discovered by a labourer in September 1879, during the laying of water-pipes beneath the military road[4] on Hadrians' wall. The hoard was found in an 'earthenware' vessel about four-feet beneath the road, near the southern face of the wall itself (Clayton 1879.257). Initially a total of 5,024 coins were recorded, however, only 1,927 remained in 1991 when the hoard was re-catalogued (Guest forthcomming) and the opportunity arose for a compositional study.

3.1.3.2 Sampling and Analysis.

A total of eighty-two coins were taken for AAS analysis. The coins were chosen to give, typically, two examples of the commoner types represented in the hoard, together with the four coins identified as 'barbar ous radiates' on the basis of style and fabric. All the coins were chosen for their relatively clean and uncorroded state, and all were clear enough to allow a full identification by the numismatist (P.Guest). A record was kept of the apparent condition and nature of any adhereing corrosion product.

A preliminary look at the data revealed a spread of values much as one would expect for the issues involved. A cursory comparison of these results with those of Cope (1974) revealed passable agreement in most cases for those elements which Cope had analysed for (mostly only silver, tin and lead). No structure was readily discernible in the data, apart from the obvious gradual reduction in silver content which is an expected feature of the period and common knowledge (Burnett 1987.113).

The only significant difference was with the composition of the 'Barbar ɔus radiates' (Plate 8). Of the four examples, the Gallienus copy had both a silver and tin content markedly higher than either of the two 'official' versions analysed (2.33% and 4.91% respectively). The coin with the Claudius II prototype had a significant zinc content (2.52%), which is considerably higher

[4] the road running from Newcastle to Carlisle. This road was built as a result of the 1745 rebellion and ran for many miles directly over the foundations of Hadrians' wall.

than any of the 'official' issues. The coin with the Postumus prototype had an unremarkable composition very similar to one of the two 'official' examples analysed, and the coin which was worn so flat as to be un-attributable, had a very high tin content (10.98%).

The 'official' coins analysed presented an apparently un-significant collection of data. The agreement between these results and Copes' gravimetric analyses was borderline, although the agreement between individual analyses of Copes is equally broad. This was, however, not surprising given the large number of types covered by the sample, and the fact that only two to four examples of each type were analysed at most. It was felt that the purpose of the analyses was to create a body of reliable analyses against which to compare the Fenny Stratford analyses, the 'Barbarious radiates' from the same hoard and the coins of the same period from the group of site finds.

As mentioned in the introduction, this hoard was discovered in a vessel and so, we can assume, protected from the worst ravages of the surrounding environment. In order to test this assumption, each coin analysed was examined closely, and attributed to one of six corrosion condition levels. The levels are, of course, strictly subjective, but given the common origin of the coins, are at least consistent. A discriminant analysis was then run to test the appropriateness of these attributions on the basis of compositional variation. Using all the elements together, only 34.57% of the coins were grouped correctly on this assumption, strongly suggesting, in this case, that the degree of corrosion is not a significant factor governing compositional variation.

However, the fact that 65% of the variance is attributed to the first discriminant function, and that this function is strongly correlated with the silver content is significant. Further investigation of the discriminant functions shows that the second group defined is discriminated primarily by the first function. This is significant because one of the criteria for group two is the presence of visible surface silvering together with a small number of malachite ($CuCO_3.Cu(OH)_2$) deposits. The explanation for this appears to be that this group contains those coins with a high silver content, which also correlates with those coins still retaining their 'silver' wash. Although all the coins represented would have originally had such a 'silver' wash, it appears (Cope 1974 84) that the process required to form this changed from one of depletion to one of application. This is because that alloys containing (under *equilibrium* conditions) under about 8% silver cannot be silver-coated by depletion, and so a variety of application techniques appear to have been used. It is possible that silver contents below 8% could have produced 'white' metal coating if the silver was in solution with tin (or lead). The mechanical action of striking a suitably *heated* coin blank (the usual method employed in Roman mints at this time - Cope and Billingham 1968b.51) may well have resulted in a phenomena not dissimilar to 'tin-sweat'

provided that the temperature was sufficiently high to keep a sufficiently segregated tin/silver phase fluid enough to be squeezed out to the surface.

Discriminant analysis was also conducted on the data when divided into the fifty different coin types represented. The results were surprisingly interesting, correctly attributing 80.25% on the basis of all elements. When the groups that the analysis suggests the coins are attributed to, purely on the basis of composition, are studied, one finds that the divergence between the numismatic attribution and the compositional attribution is not significant. All the coins from the mint of Rome remain a compositional group regardless of issue or emperor. One of the commemorative coins of Claudius II, of unknown mint, is lumped with the commemorative issues of Milan, whereas the other remains discrete. Furthermore, the issues of the Gallic empire are kept consistently separate from those of the Central empire. The four barbar ous radiates also remain a discrete group, with the exception of the Postumus copy which is re-attributed to one of the Tetrician groups.

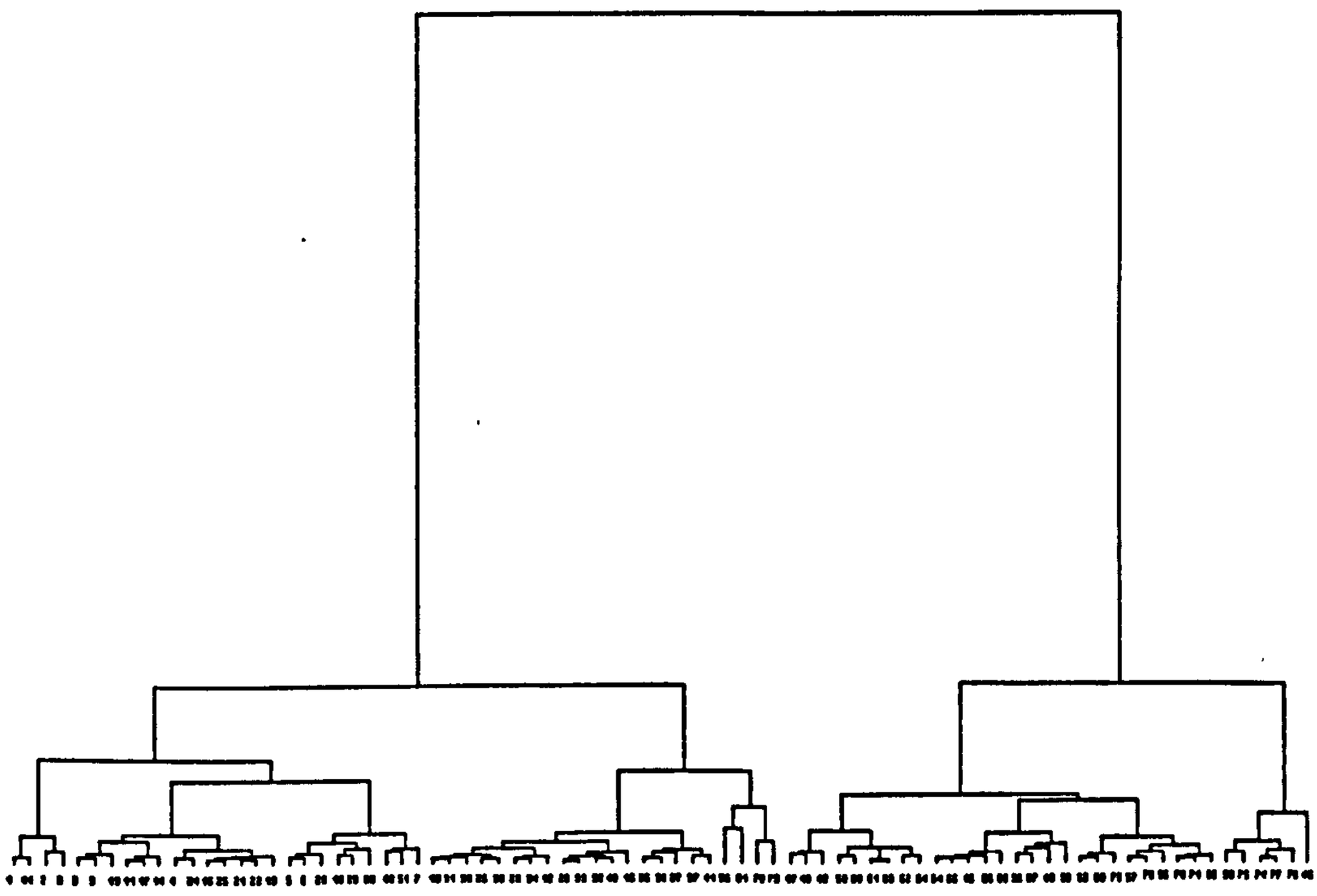


FIG.22. DENDROGRAM OF MAJOR COMPONENTS

The success of this discriminant analysis prompted further investigation. Firstly, Ward's method cluster analysis was conducted on the log-transformed data, initially on all elements, and then on major elements (Ag, Sn, Zn and Pb) and trace elements (Sb, As, Ni, Fe, Co, Cr, and Au). The resultant dendrograms all show a clear division between the products of the Central empire and the Gallic empire (Figs.22 and 23). Within the Central empire group there is some definition

between the issues of Gallienus and the issues of Claudius II, based both on the major components and the minor component.

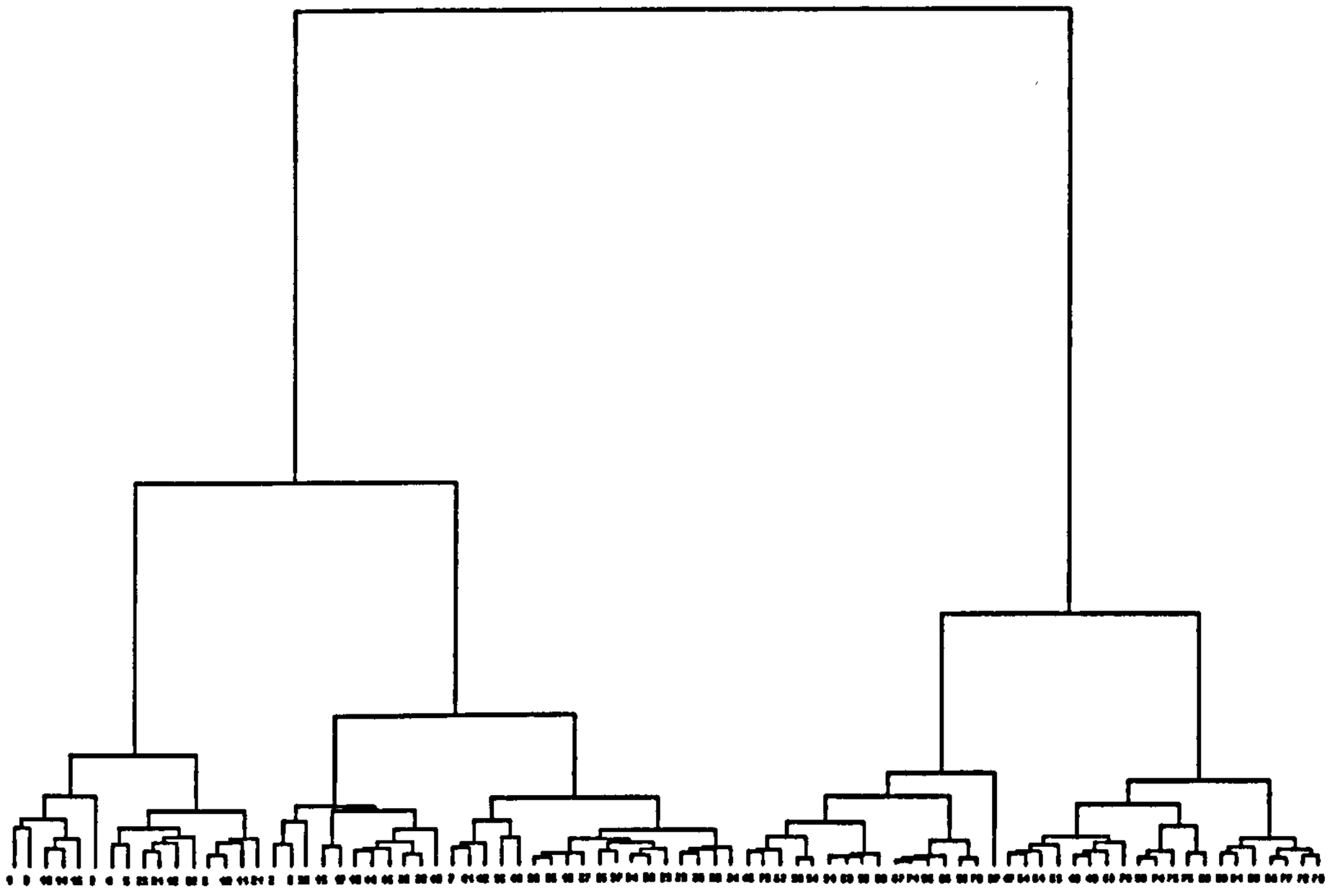


FIG.23. DENDROGRAM OF MINOR COMPONENTS.

In order to clarify the situation a principal components analysis of the covariance matrix was conducted on the same data sets. The results (Figs.24, 25 and 26) clearly confirm the dendrograms whilst introducing greater clarification. The clearest groupings are those using the major (controllable) components, this is not only true for the two main groups, but also for the separation of the issues of Gallienus (denoted by 'G') and Claudius II (denoted by 'C'). The latter is unsurprising given the marked reduction in silver content between the two reigns. Furthermore, the variable loadings tell us that the first component (the horizontal axis) is mainly influenced by the tin content, and it is the second component which is influenced mainly by the silver content. It is interesting to note that the four 'barbar ous radiates' (denoted by '*') are fairly well lumped in with the Central issues when using the major components, yet when we look at the PCA of the minor components (Fig.26) they are firmly with the Gallic issues. Furthermore, the PCA using all components (Fig.24) places them rather disparately (but discretely) in the 'no-mans land' between the two! The reasons for this will be discussed in chapter five.

The PCA of the trace elements group the Gallic issues far more discretely than the Central issues, which are, themselves, more discretely grouped by the major components. This suggests

that the level of control exercised by the moneyers on the amounts of lead, tin, silver and zinc used in the issues of the Central mints is a more important factor in the grouping of these coins than the concentrations of the un-controllable trace elements (whose presence was unknown and relates to the origin of the metals which were controlled). Furthermore, the fact that the exact opposite is true of the Gallic issues, suggests that the 'supply pool' for the metal going into these coins is less disparate than the 'supply pool' available to the Central mints. This model would seem logical given that the coins of the Central empire were issued by five mints; Rome, Milan, Siscia (Croatia), Cyzicus (Turkey) and Antioch. The Gallic emperors issued coins from two mints (Burnett 1987.123); Lyon and Cologne (more probably Trier). Obviously a much more discrete grouping would be expected from coins coming from only two mints, and which, being relatively close geographically, would be drawing upon a similar 'supply pool'. The numismatic implications of this work will be discussed fully in chapter five.

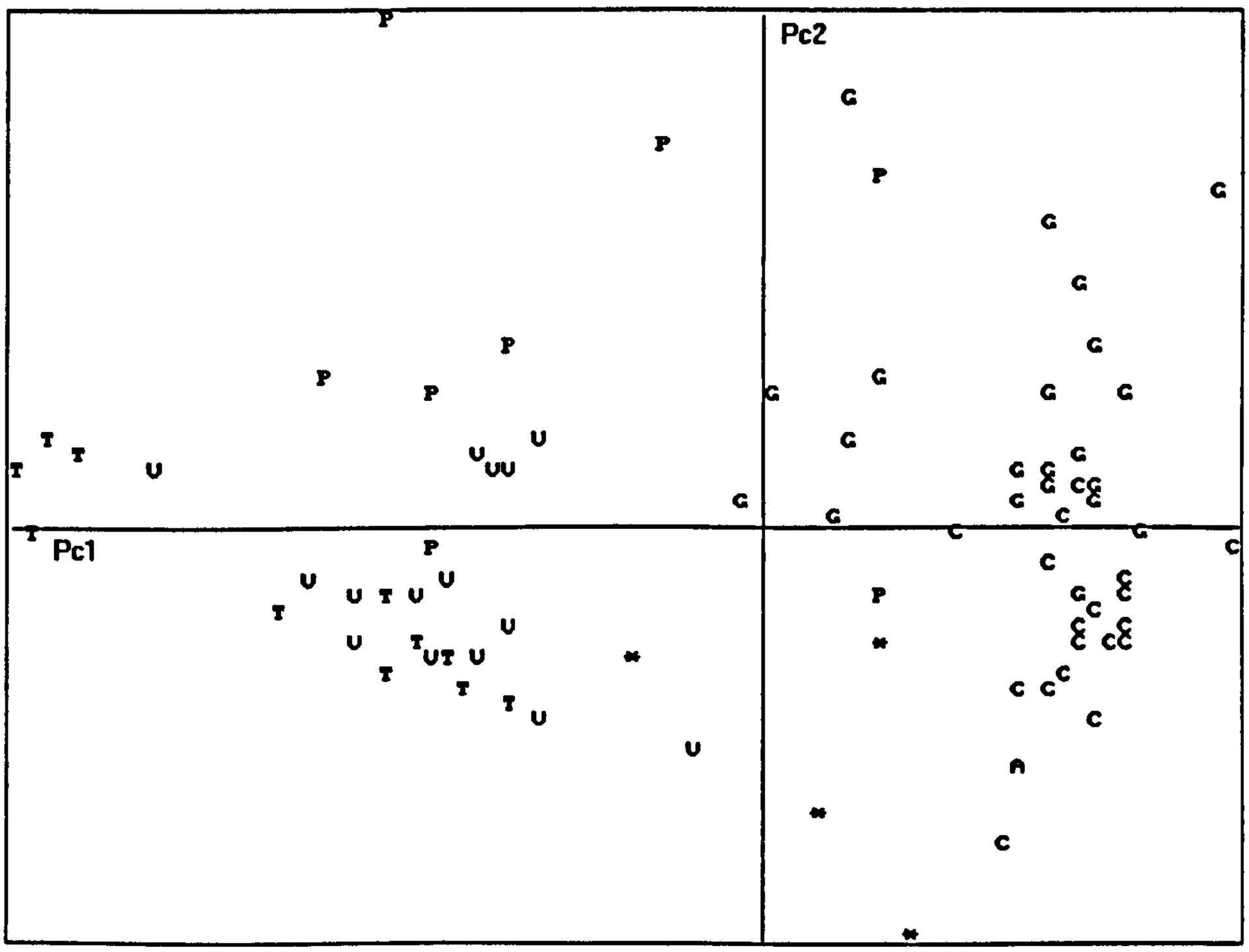


FIG.24. PCA PLOT OF ALL COMPONENTS

Key to PCA plots:

G issues of Gallienus (including Salonina)
C issues of Claudius II (including Quintillus)
P issues of Postumus (first Gallic emperor)
V issues of Victorinius (second Gallic emperor)
T issues of Tetricius I and Tetricius II (last Gallic emperors)
A issue of Aurelian (pre-reform)
***** 'Barbar. ous radiates'

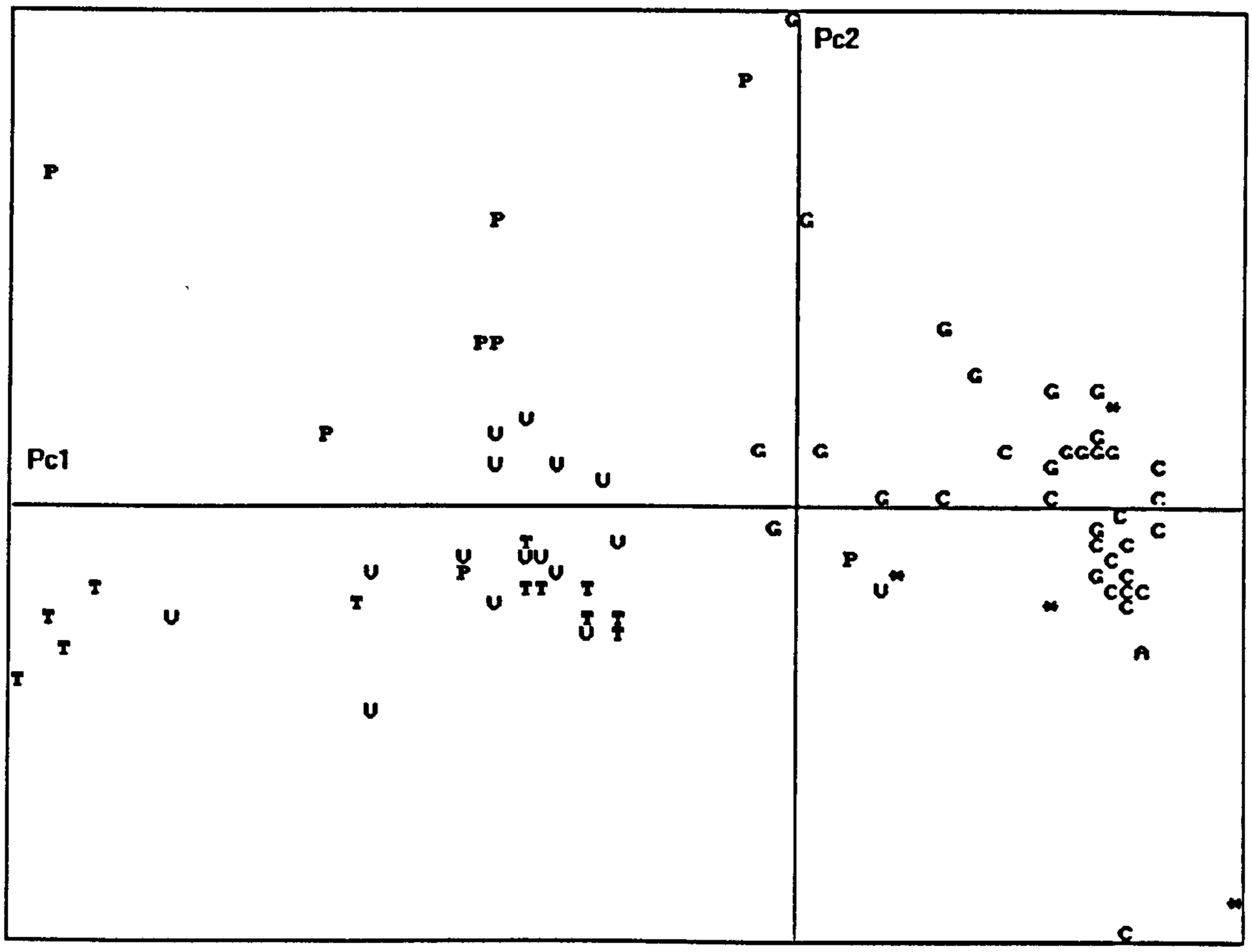


FIG.25. PCA PLOT OF MAJOR COMPONENTS.

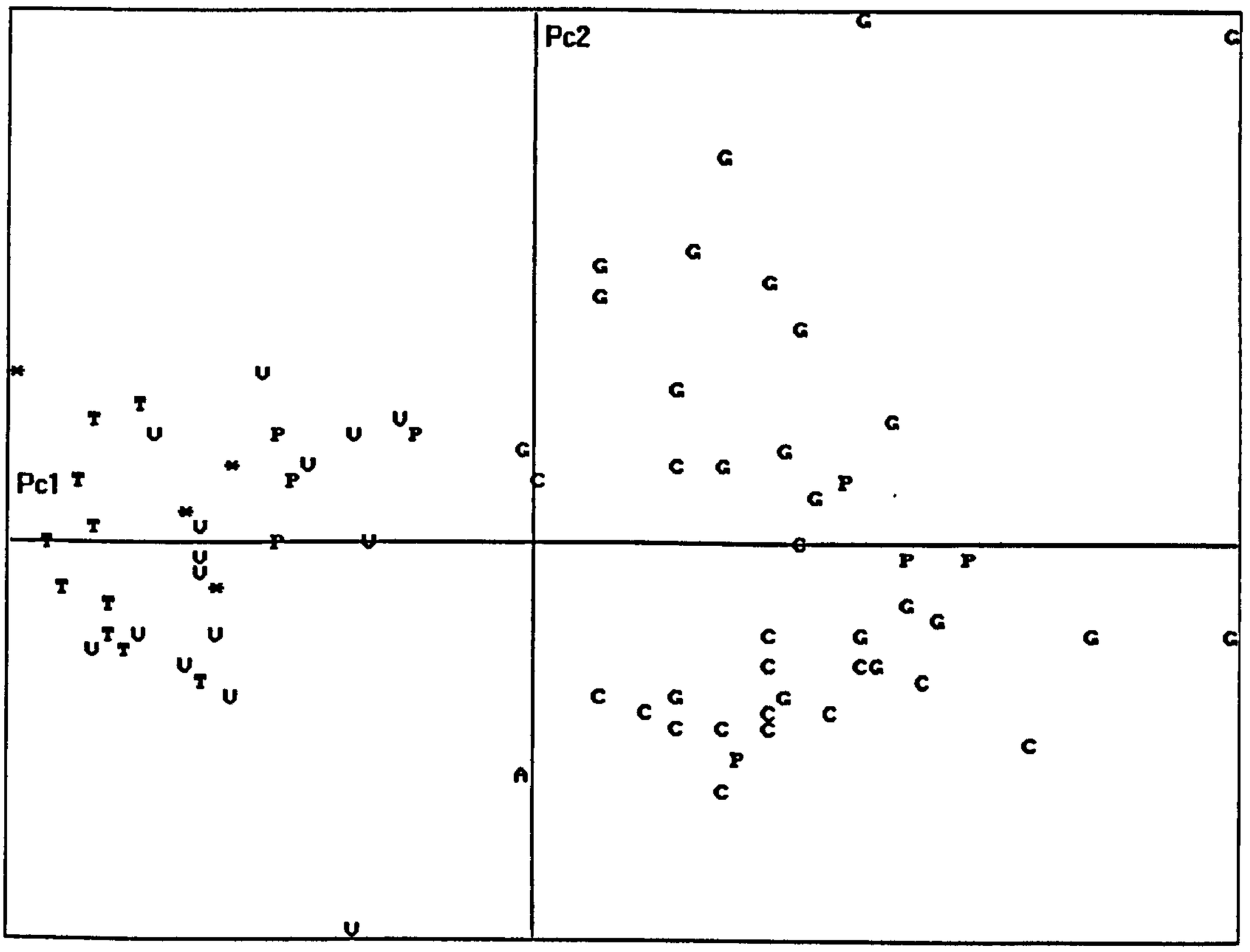


FIG.26. PCA OF MINOR COMPONENTS.

3.1.3.3 Discussion of analysis.

The use of standard multi variate techniques on the log-transformed data has disclosed a structure to the data which was not apparent before. This structure is numismatically significant, showing compositional traits which have not been detected in previous analyses (such as Cope 1974 or Ziegler 1983). These previous analyses have concentrated on the major components only, looking for levels of 'fineness' in the silver and sometimes lead:tin ratios (Cope 1974.119). Indeed, many investigations neglect to include minor and trace components. Furthermore, all the coins analysed came from the same hoard and it has been established with reasonable certainty that the variation encountered is due to the alloying processes and sources of metal.

3.1.4 General Discussion.

The preceding sections looked in detail at the traits within the two separate data sets, and have confirmed that the traits discovered are indeed a function of the alloying processes and metal source, and not the result of cleaning or corrosion. The results are interesting, suggesting that a considerable degree of control was being exercised in the production of Barbar.ous radiates, and that numismatically significant variation can be found within the 'official' issues of the period.

The next stage was to amalgamate both data sets, and to augment these with the analyses of similar material from the group of site-finds from Market Deeping (see section 3.4). This done, another set of PCA analyses was conducted.

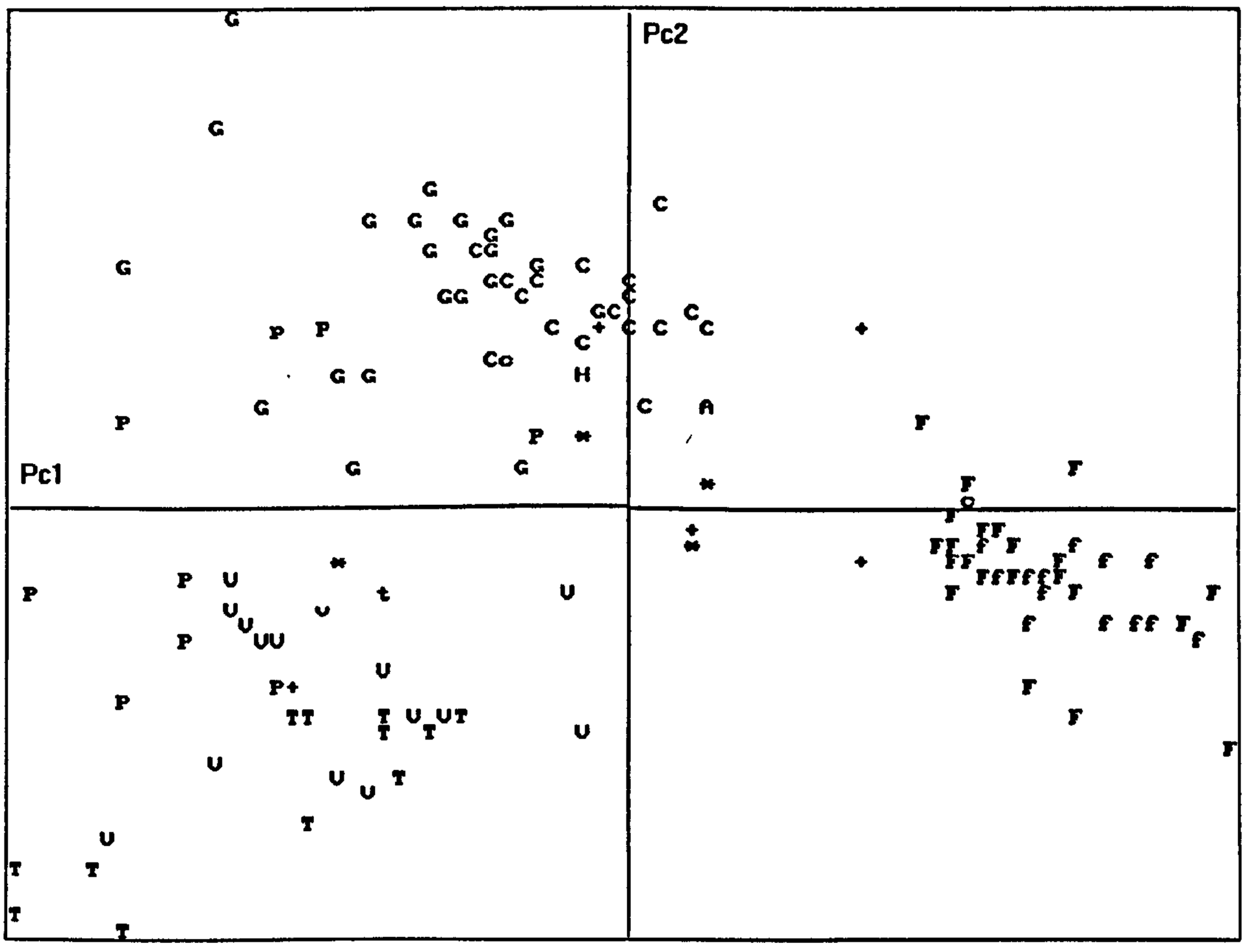


FIG.27. PCA OF ALL RADIATES USING ALL ELEMENTS.

Key:

G Gallienus **C** Claudius II **P** Postumus (Gallic)
V Victorinus (Gallic) **T** Tetricii (Gallic) * Walbottle Barb.Rads.
F Fenny Blanks **f** Fenny pellets **c** Deeping Claudius II
p Deeping Postumus **t** Deeping Tetricus I
v Deeping Victorinus + Deeping Barb.Rads.

The aim of this analysis was to discover if there is any relationship between the Fenny Stratford material (being the raw materials for the production of 'Barbar ous radiates') and the

struck radiate copies in the Walbottle hoard and in the site finds. It is also of interest to see how well the heavily corroded site finds fit in with the well preserved hoard material, although this aspect will be covered more fully later.

The initial PCA plots using all elements, and then majors and minors separately, proved inconclusive (and disappointing). The plot of all elements (Fig.27) shows little more than the discrete nature of the Gallic radiates, the Central radiates and the native British radiate copies from Fenny Stratford. The struck radiates from both Walbottle and Market Deeping (* and +) seem to be scattered between the three main groups, with, maybe, a fondness for the middle ground. It is, perhaps, significant that one of the Market Deeping radiates (of Claudius II) sits firmly within the Fenny Stratford group, whereas the other Market Deeping radiates sit where one would expect them to. Likewise, the fact that almost all the radiate copies appear to sit either within one of the two regular groups, or tend towards the Fenny Stratford group, would suggest that either their attributions as 'Barbar ous radiates' is incorrect, or that 'Barbar ous radiates' were 'over-struck' on official radiates. Furthermore, it would seem that some radiate copies do indeed have a composition more akin to the Fenny Stratford material than to either of the official groups.

Because this initial exploration of the data remained inconclusive it was decided to adopt the inverse strategy and conduct a discriminant analysis on the same data set. This time the coins were grouped by mint or their status as radiate copies/Fenny Stratford material and two separate analyses were run. Both runs used all elements. The first included the Fenny material and the struck radiate copies as one of seven groups. This gave a 79.26% correct attribution, with the F values telling us that the zinc, tin, nickel and lead were the strongest discriminating components (86.96% of the variation being clearly in the first two functions). Next, it was decided to run the analysis excluding all the Fenny Stratford material to see how many of the struck radiates were correctly grouped together, and which components are useful in discriminating between the official coin groups and the radiate copies. The results gave a 69.57% correct attribution, with five out of nine struck radiate copies being correctly attributed. Of those which the statistics place in other groups, one goes to Rome, two to Cologne and one to Trier. The leaning towards a Gallic origin is obvious. However, it should be pointed out that the level of correct attribution is no greater in any of the other groups, excepting Cologne, which has a 96.3% correct attribution. The Fenny material is all correctly attributed, which is unsurprising given that we are dealing with the output of a single work-shop. It is encouraging to note that the official issues of Trier, which number the same as the struck radiate copies, has the same number correctly attributed.

The two official radiates from the Market Deeping site finds which were sufficiently un-corroded to allow attribution to a mint (one to Trier, the other to Cologne) are not attributed to

either of their respective mint groups, and the radiates which were too heavily corroded to allow attribution to mints (which were therefore put in a ? group), remain in a separate category, except for one, which is re-attributed to the radiate copy group. This separating out of some of the Market Deeping material may be due to its highly corroded condition, and will be investigated further in a later section.

The components responsible for this level of discrimination are tin, cobalt and nickel (F values of 19.67, 8.667 and 6.921 respectively with 100% significance). These components are responsible for 89.91% of the variance in the first three functions (77.64% in the first two).

Consequently it was decided to use this information to conduct a final PCA analysis using all the material, but only those components which the discriminant analysis tells us are the best in discriminating between official radiates and their copies. The plot in Fig.28 shows the fist two components (accounting for 84.49% of the variance) using zinc, tin, cobalt and nickel as our variables.

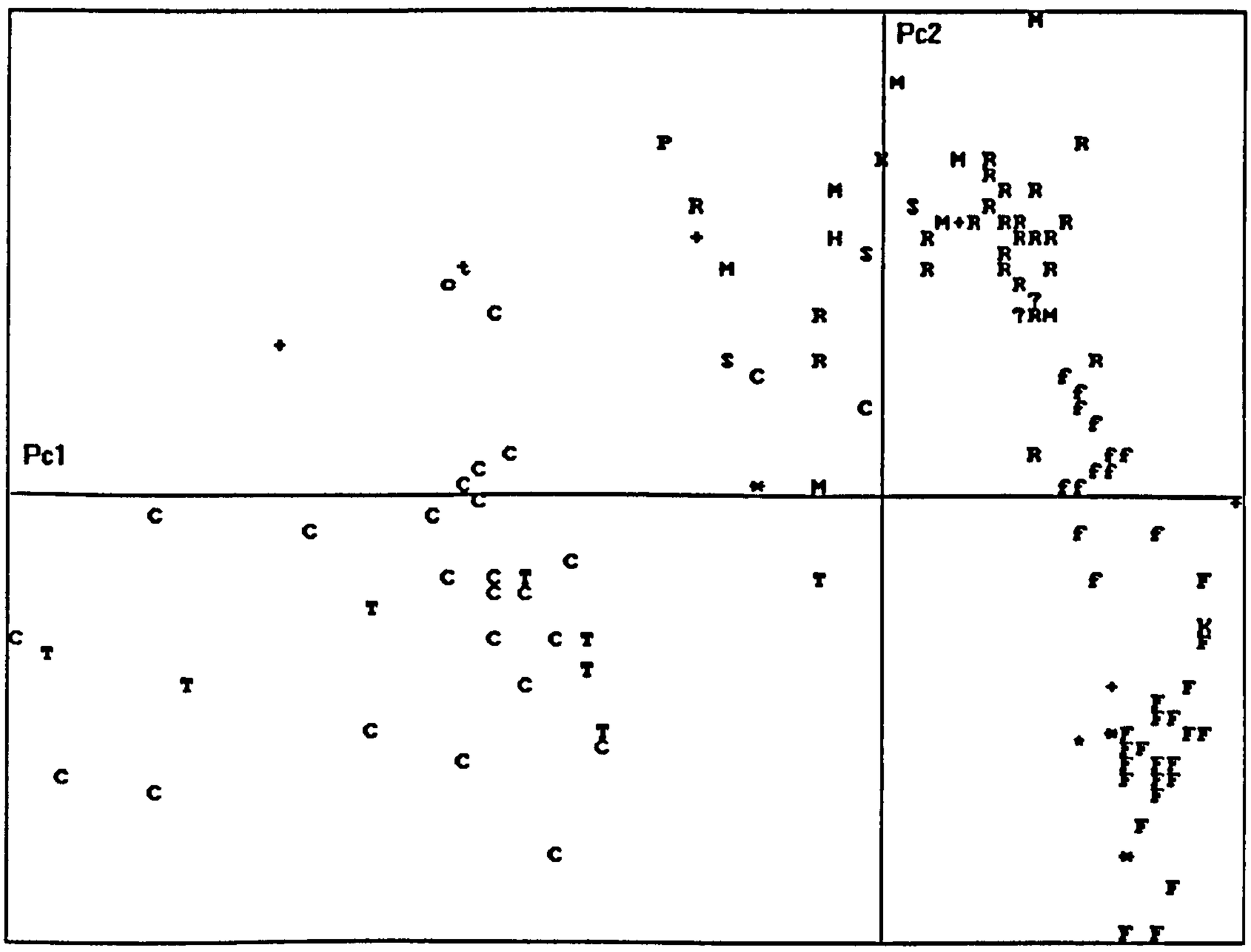


FIG.28. PCA OF ALL RADIATES USING ZN, SN, CO AND NI.

Key: R Rome M Milan S Siscia C Cologne T Trier
F Fenny blank f Fenny pellet * Walbottle Barb.Rad
+ Deeping Barb.Rad. ? Unknown K/c Deeping Claudius II
t Deeping Tetricus I P Deeping Postumus

According to the variable loadings (Table 5) the Fenny Stratford/struck radiate copy group is separated from the Central empire mint group by the cobalt and nickel levels, and from the Gallic mint group by the zinc and tin levels.

Element	Pc1	Pc2
Zinc	105	-91
Tin	174	45
Cobalt	21	88
Nickel	-2	57

TABLE 5. VARIABLE LOADINGS FOR FIG.28. (X 100).

The Gallic mint group becomes more discrete if the zinc is removed from the analysis, this tends, however to reassign some of the struck radiate copies from the 'radiate copy' group into the Central empire mint group. This confirms that zinc is an important component in discriminating between official radiates and their copies. It appears to be a combination of the zinc, nickel, tin and cobalt levels which are capable of distinguishing the radiate copies from their official prototypes. The archaeological interpretation of these findings will be discussed in chapter five.

3.2 Constantinian Copies: The Tingrith Hoard, the Richborough Hoard and the Bancroft Villa Hoard.

3.2.1 General introduction

This section deals with our second group of copies and addresses a number of different problems. Firstly, the Tingrith hoard offered a chance to analyse a selection of well preserved Constantinian issues from selected north-western mints (including London) and to study the degree of consistency in the composition of a specific issue from a specific mint. It was also possible to investigate the existence of copies at this early period, the existence of which has only recently begun to be appreciated (Reece. pers.comm.).

Secondly, the results of the analysis of the well preserved Tingrith material could then be compared with the analyses of the poorly preserved Richborough hoard, which consists of very similar material. The Richborough hoard itself provides the subject of a study dealing with the spatial aspects of corrosion and how composition can be affected by location within a hoard. This will be discussed in chapter four.

Thirdly, the Bancroft villa hoard provides an example of a hoard which has been numismatically investigated by Cathy King (1981). This hoard comes from the main period of Constantinian copying and as such is useful for a more in depth look at the compositional differences between copies and official Constantinian issues. The comparison between this hoard material and similar issues from Market Deeping will also be discussed.

3.2.2 The Tingrith Hoard.

3.2.2.1 Introduction

On 20th June 1961 a hoard of over 3,000 copper alloy coins were discovered in a sand quarry at Tingrith, Bedfordshire. The coins had been buried in a ceramic vessel, with another vessel inverted over the neck of the first to exclude the soil. The fabric of the vessels is coarse, with shell inclusions and mottled grey and orange surfaces. The report of the circumstances of the find states that,

> "....the bucket of the mechanical excavator had broken into a pot-full of coins."

This suggests that the coins were sealed within the vessels up until the discovery. The vessels had been placed in a small pit dug to a depth of about a metre and a marker stone appears to have been placed on the surface of the backfilled pit (Deacon 1990).

The hoard consists of issues of the house of Constantine covering the period 318-337 AD and are attributable to thirteen mints. However, over 80% of the coins are the issues of the mints of London and Trier. This is in keeping with other hoards of the period, the majority of which

comprise predominantly the issues of Trier, London and/or Lyon (Deacon 1990, Reece 1987 119-123). However, it is increasingly apparent that local copying of these issues was practised to a considerable degree, and with notable proficiency. Indeed, it is sometimes extremely difficult for even the experienced eye to differentiate the official coins from the copies. Furthermore, it has been suggested that some of the extremely rare and obscure variations of commoner types may in-fact be the products of unofficial or semi-official mints (Reece 1992).

3.2.2.2 Sampling and Analysis

The initial analysis was conducted on a group of 689 coins which had been loaned to a colleague for numismatic recording. This group of coins was sampled specifically to look at the products of the most prolific north-western European mints; London, Trier and Lyon together with a number of coins that, although of good workmanship, differed in a number of ways from the standard issue normally encountered. These questionable coins are, because of their competent style, usually regarded as variants on official issues. If this is true then they should exhibit some compositional similarity with the *bona fide* issues of the same mint and period. The overall aim was to gain a body of *reliable* analyses of coins of this period issued by the commonest western mints. Following the establishment of this base-line it was then possible to look for structure within the data set and relate this structure to the origin of each coin analysed.

Thirty-eight coins were selected from the group and sampled by drilling in the usual fashion. The drillings were then analysed by AAS. The resultant data were initially explored by standard descriptive techniques. It quickly became apparent that the silver, lead and tin contents varied significantly between the three main mints represented.

Plotting the percentages of silver against the lead shows clear clustering into mint-related groups (Fig.29). A Chi-squared (Shennan 1988.65) probability of 14.7 at eight degrees of freedom suggests that the null hypothesis that the ratios of silver and lead in the coins were dissimilar is invalid. This is not surprising given their metallurgical affinity (Cope 1972.17). The silver values generally fall between 0.5% and 1.5% (slightly below that reported by Cope) with a range of ±8% (three coins) falling above and ±25% (nine coins) falling below. The two highest silver values belong to coins of the same issue (RIC 213) with the third coin of that issue analysed having the fourth highest silver value. The issues from the mint of London exhibit the most homogeneous group, with both issues (RIC 295 and 296 - PROVIDENTIAE CAESS issues of Crispus and Constantine II respectively) clustering at the ±1% mark. Three coins from the London mint fall together around ±0.5%, one of which is a clear copy of RIC 220 (BEATA TRANQVILLITAS issue of Constantine I), this would suggest that the other two coins (RIC 295 and 296) are irregular also, despite their seemingly regular appearance.

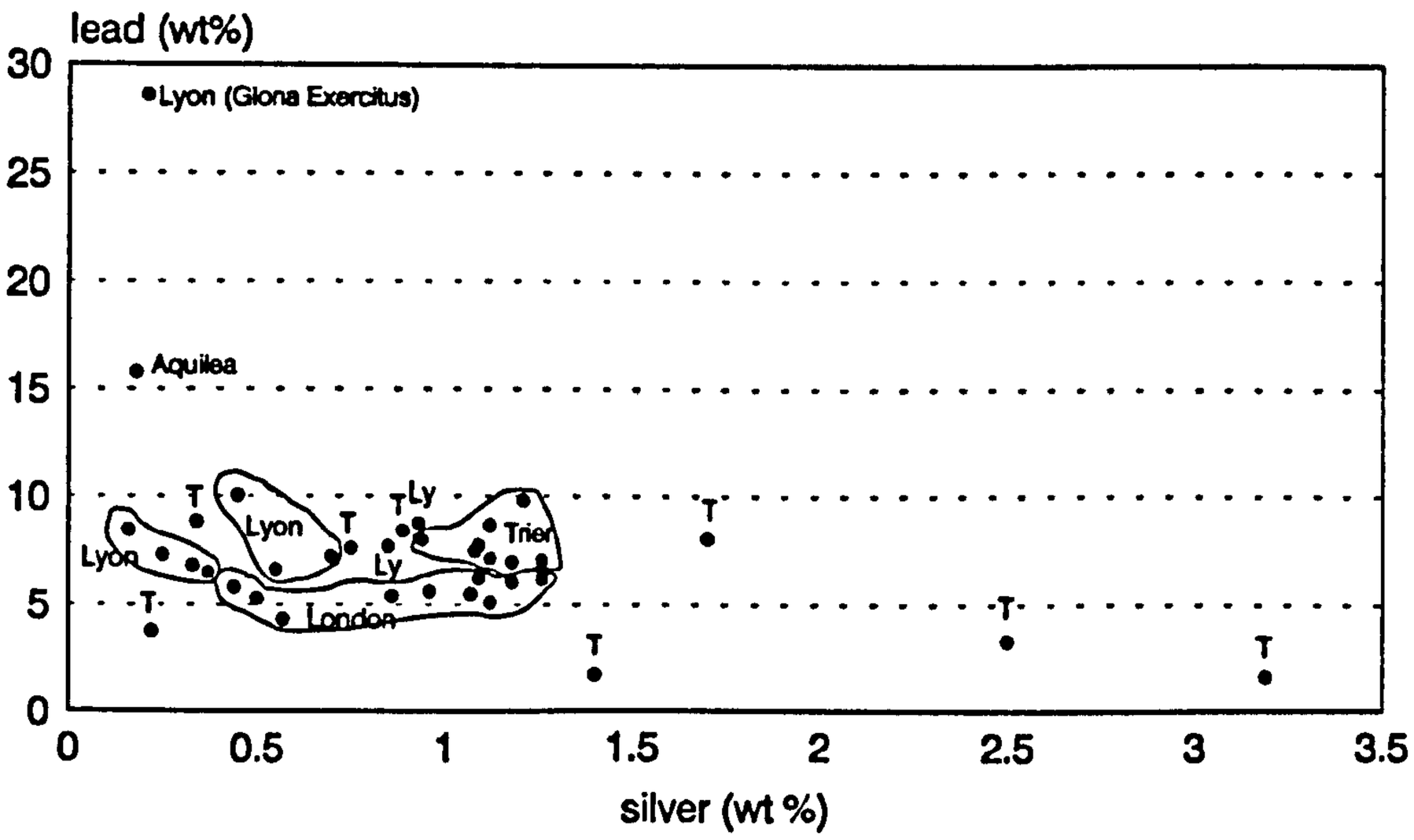


FIG.29. PLOT OF SILVER AGAINST LEAD VALUES FOR TINGRITH SAMPLE.

The single coin from Aquilea readily stands apart on the basis of its silver and lead content, as does the GLORIA EXERCITUS issue (Constantine II - probably irregular). This is even more apparent when the lead and tin values are plotted together (Fig.30).

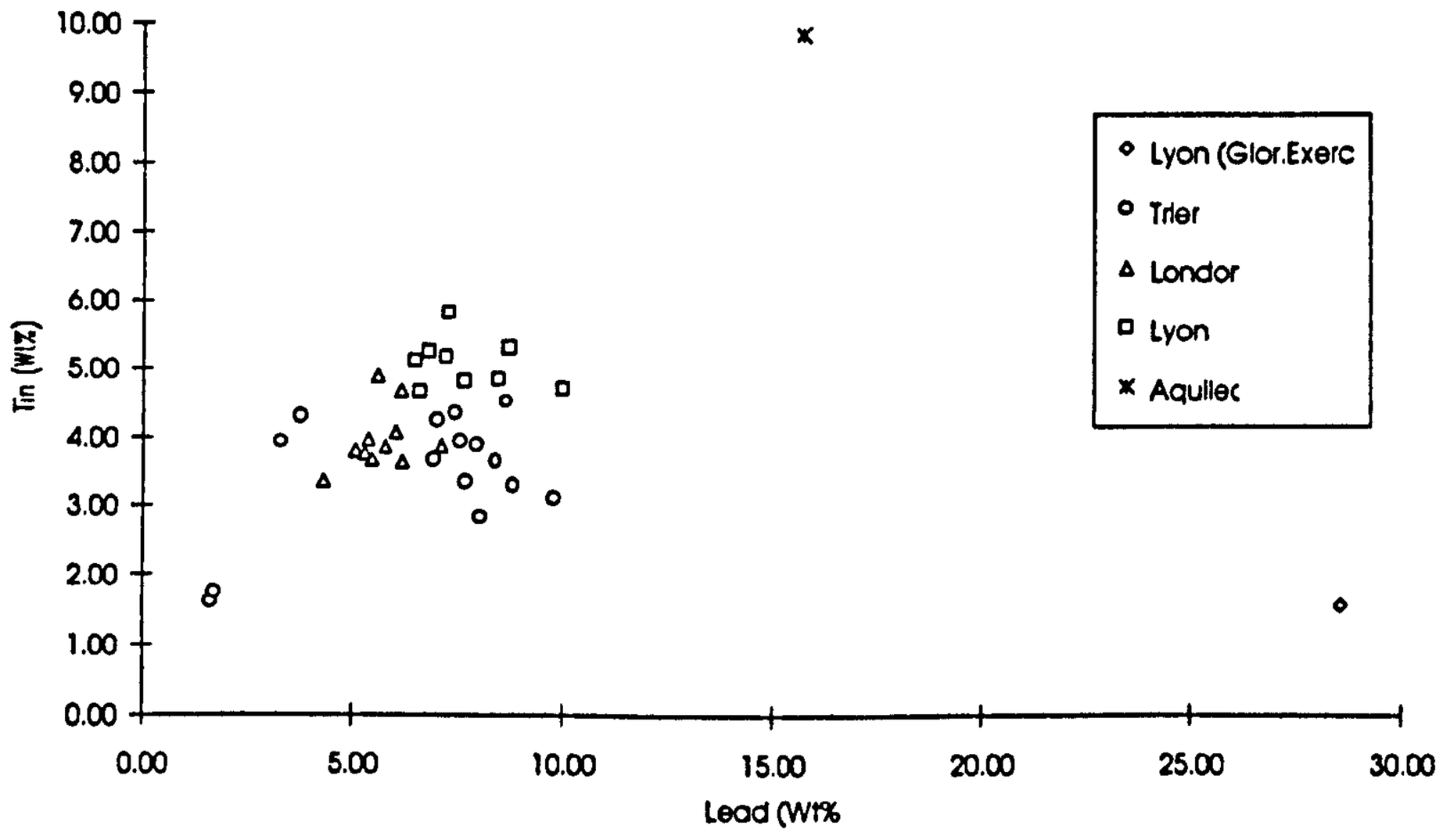


FIG.30. PLOT OF TIN AGAINST LEAD VALUES FOR TINGRITH SAMPLE.

Most of the coins cluster in a discreet group of 5 - 10% lead and 3 -5.5% tin with three outsiders, one being the GLORIA EXERCITUS issue, the other two both being RIC 213 issues of Trier which also have low lead (<2%). A lead-tin correlation coefficient (Shennan 1988.114) of 0.47, although not high, is nevertheless significant to the 99% level of confidence. This would suggest that the lead and tin were added to the metal mixture already alloyed in the way suggested by Cope (1968.138). However, it is also of interest that the tin:lead ratio appears to vary between the mints investigated. Trier operates on a ratio of about 2:1, London and Lyon, on the other hand, used a ratio closer to 1.5:1. The tendency for the products of the different mints to cluster on these two constituents is also apparent from the plot, but is less marked than for the silver and lead.

Similar plots drawn for the minor components show that the mint of Trier is responsible for coin issues with the highest iron and nickel contents, but also exhibits the greatest variation (Fig.31). The single coin of Aquilea stands out because of its high nickel but low iron content. This Aquilean coin is aberrant to this collection, since it is a single possible example of the output of that mint. No conclusions about the *normal* output of this mint can be drawn at this point. Both the mints of Lyon and London are notable for their lack of variability in these metals. Arsenic, antimony and zinc appear to be fairly evenly distributed across all groups, with the mint of Trier and the one 'GLORIA EXERCITUS' issue having the highest antimony values.

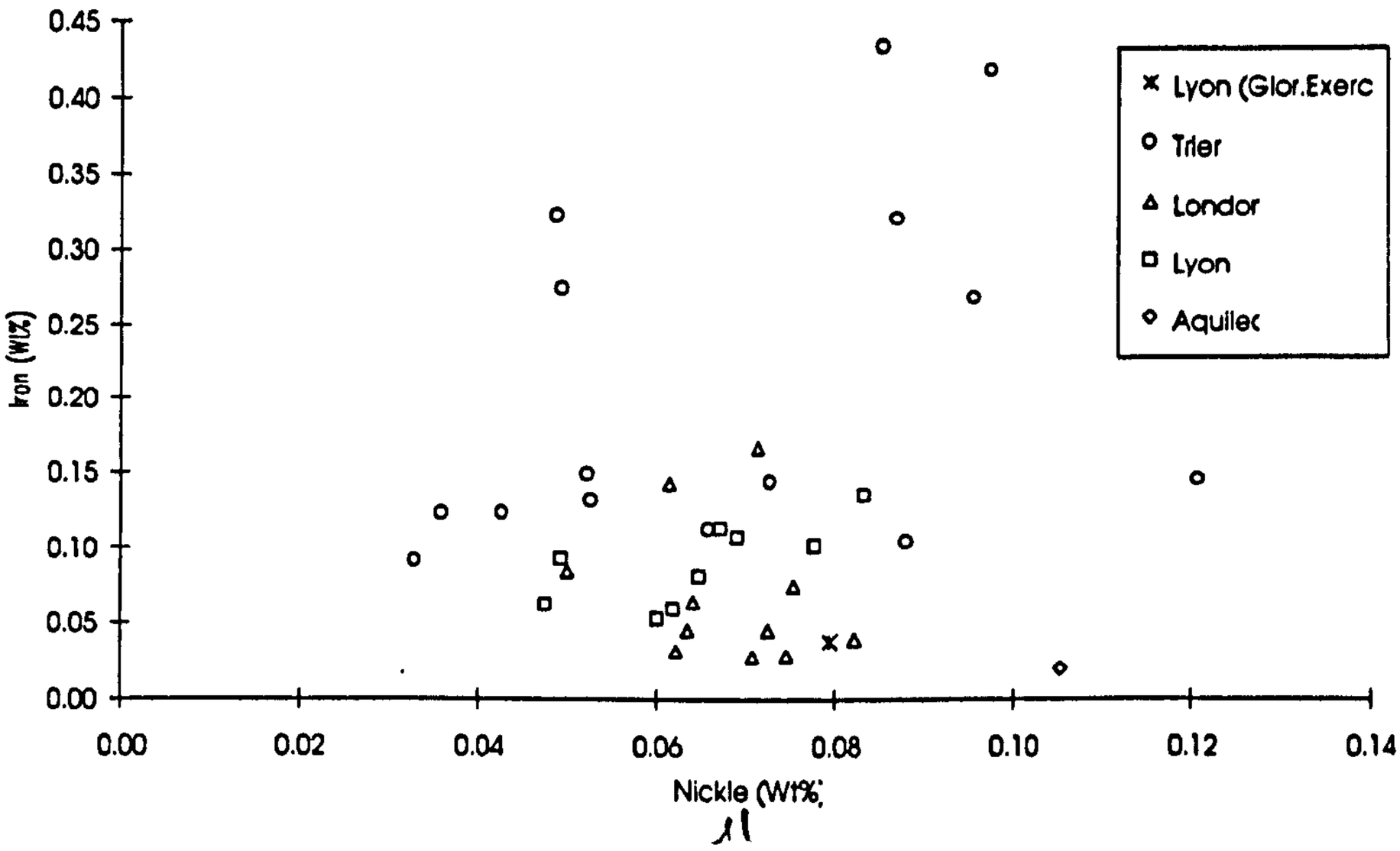


FIG.31. PLOT OF NICKEL AGAINST IRON VALUES FOR TINGRITH SAMPLE.

The next stage in the data exploration involved the multivariate techniques, exploring the relationships between all compositional variables at once. Principal component analysis (PCA) of the covariance matrix was employed (Wright 1992) on all transformed data as well as on two subsets. These consist of the 'major' components (silver, lead and tin) and the trace components (nickel, iron, zinc, gold, arsenic and antimony). When the first two principal components are plotted for each set of data each of the three mints are clearly clustered. However, it is interesting that the best and most clearly defined set of clusters is produced from all variables together (Fig.32). No increase in resolution is gained by the division of the data into subsets. Perhaps of more obvious importance is the existence of a fourth, rather diffuse cluster including the coin regarded as an 'irregular' copy with the coins listed as 'as RIC No....'. This strongly suggests that the coins of 'good' style but exhibiting oddities of type are also 'irregular' copies.

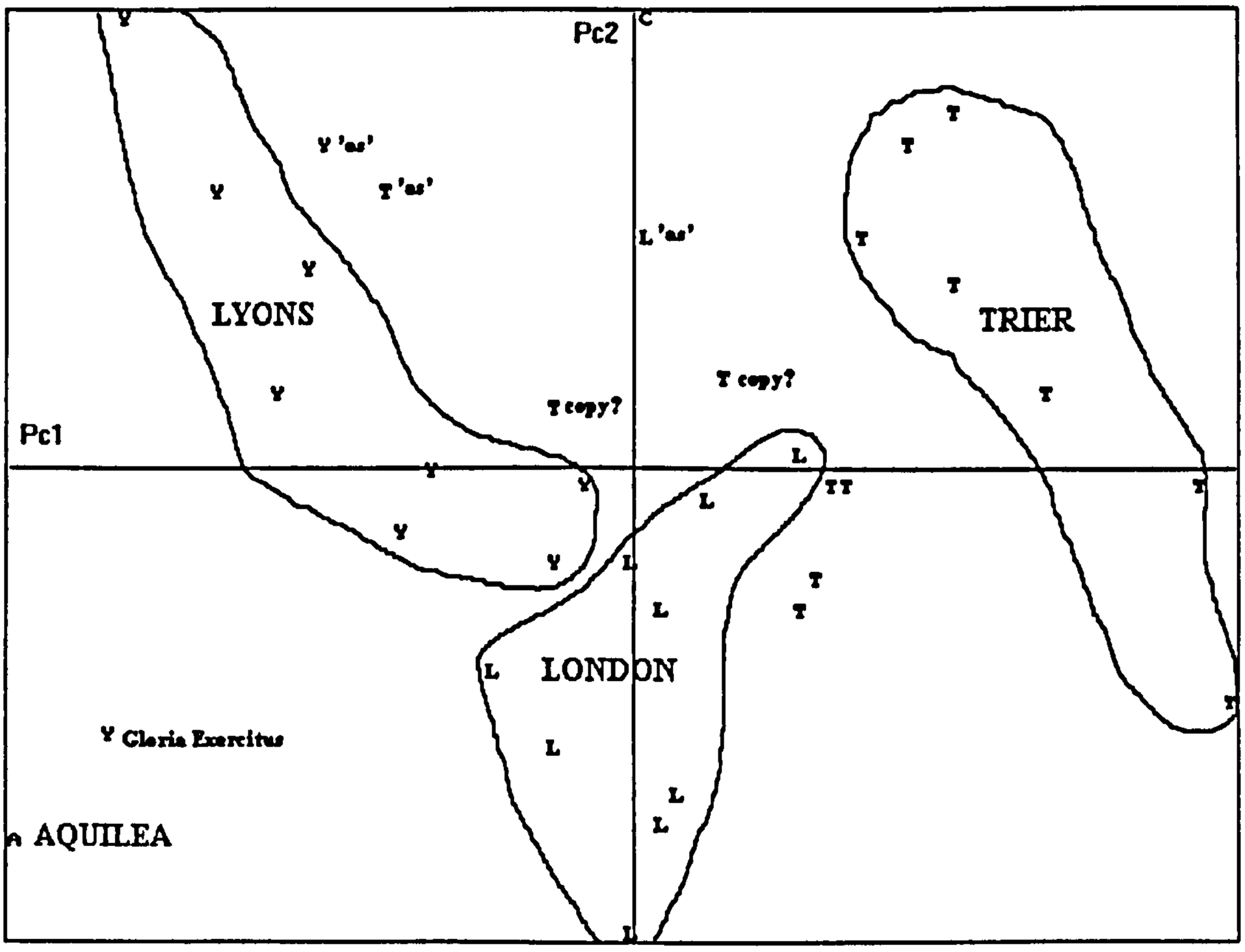


FIG.32. PCA PLOT FOR ALL COMPONENTS.

In order to confirm the validity of the PCA clusters a k-means cluster analysis was run (Wright 1992). This largely confirmed the attribution on the basis of mint, although grouped all the 'copies' with the issues of the mint of Lyon (regardless of the mint marks born by the copies).

Group 1	Trier (1-10 and 22,23 and 25), London (16).
Group 2	Aquilea and the Gloria Exercitus issue.
Group 3	London (11-15,17-20), Lyon (26 and 32).
Group 4	Trier (6), Copies (21,24,35,37), Lyon (27,28,30,31,33,34,35).

TABLE 6. TABLE OF K-MEANS ANALYSIS ATTRIBUTIONS.

As a further check it was decided to run a discriminant analysis using all variables but specifying six groups; Trier, London, Lyon, Aquilea, the GLORIA EXERCITUS issue and the 'copies'. This analysis confirmed all expected groupings, including the attribution of copies. Furthermore it also suggested that a coin ostensibly of Trier is more likely to be a copy on the basis of its composition alone (No.10).

Discriminant analysis was also of value in suggesting which metals in the composition are largely responsible for the groupings (Table 7). The three most important metals, as initially suggested, are (in descending order of importance); tin, silver and lead. Tin is of considerably greater significance however, having the greatest variability between groups. The iron is also picked out as having significant variability, but not in a way that affects the attribution of coins to the groups specified.

Silver	7.986
Lead	4.259
Nickel	.7843
Iron	11.97
Zinc	4.003
Arsenic	2.672
Antimony	2.167
Tin	11.05

TABLE 7. TABLE OF F VALUES FOR CONSTITUENT METALS

The next step involved the analysis of a group of coins from the same hoard, but consisting of pieces which had been singled out as being in some way different to the majority of coins of a particular type. The results of this particular analysis were added to the previous set, and a PCA conducted on the transformed data. From the foregoing analysis, it was expected that these 'odd' coins would be grouped with the similarly 'odd' coins in the first data set, especially considering that they came from the same hoard. However, the expected differentiation was not forthcoming.

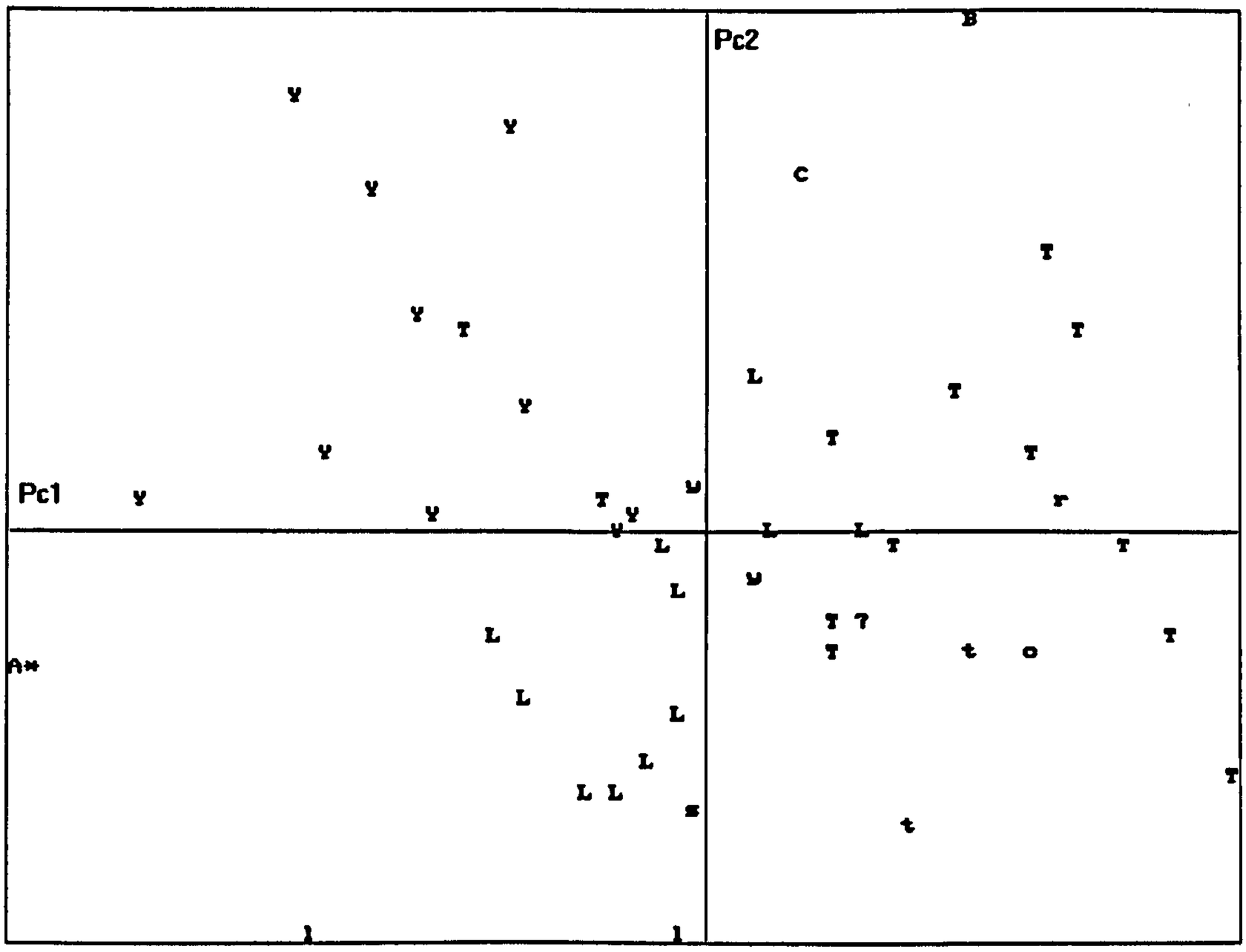


FIG.33. PCA PLOT OF 'ODD' COINS AND INITIAL SAMPLE.

Key:

T	Trier	**L**	London	**Y**	Lyon	**A**	Aquilea
t	'odd' Trier	**l**	'odd' London	**y**	'odd' Lyon	**s**	'odd' Siscia
r	'odd' Rome	**c**	'odd' Ticinium*		'odd' ?	**?**	'odd' Rome?

B Bancroft villa hoard coin of Trier.

As can be seen from Fig.33. the addition of more data does little to strengthen the case for a clear distinction between the securely attributed coins and those of an 'odd' aspect. However, it is significant that a general agreement is achieved between the coins of a particular mint. This analysis would tend to suggest that the 'odd' coins are not, after all, always 'irregular' issues or copies. In other words, that the differences between the two are, at this period, so minute that it is almost as difficult to tell them apart compositionally as it is stylistically. This is not to say that there are not significant differences. A discriminant analysis run on the same data certainly suggests that some of the 'odd' coins are compositionally different to their supposed mint fellows and similar to the other suggested copies, which are themselves all confirmed as being compositionally different. It is just that these differences are so small and varied that PCA is hard put to group these coins in a convincing fashion.

A further PCA analysis was conducted taking subsets of elements suggested by the F values given by the discriminant analysis. These were arsenic, cobalt and tin (F values of 5.676, 10.84 and 7.224 respectively). The resultant plot (Fig.34) is interesting in that it groups each of the

three main mints quite convincingly and places most of the 'odd' coins in a separate cluster well away from them. Closer investigation reveals that the nicely discrete London group also contains the known 'copy' and one of the 'as' coins (No.37) from the initial analysis, together with the two coins which the discriminant analysis places in the 'copy' group (Nos.14 and 42). This was rather perplexing until it was noticed that it is predominantly the London group which contains a number of the coins which are likely to be copies. Both the Trier group and the Lyon group contain a coin each which are 'odd' in some way, these would, however, appear to be compositionally similar to the regular issues of these mints. It would appear that the London coins have arsenic, cobalt and tin levels which are very similar to those found in the majority of the likely copies. The explanation seems to be that they would probably share a common metal supply pool, assuming that the copies are the products of British workshops.

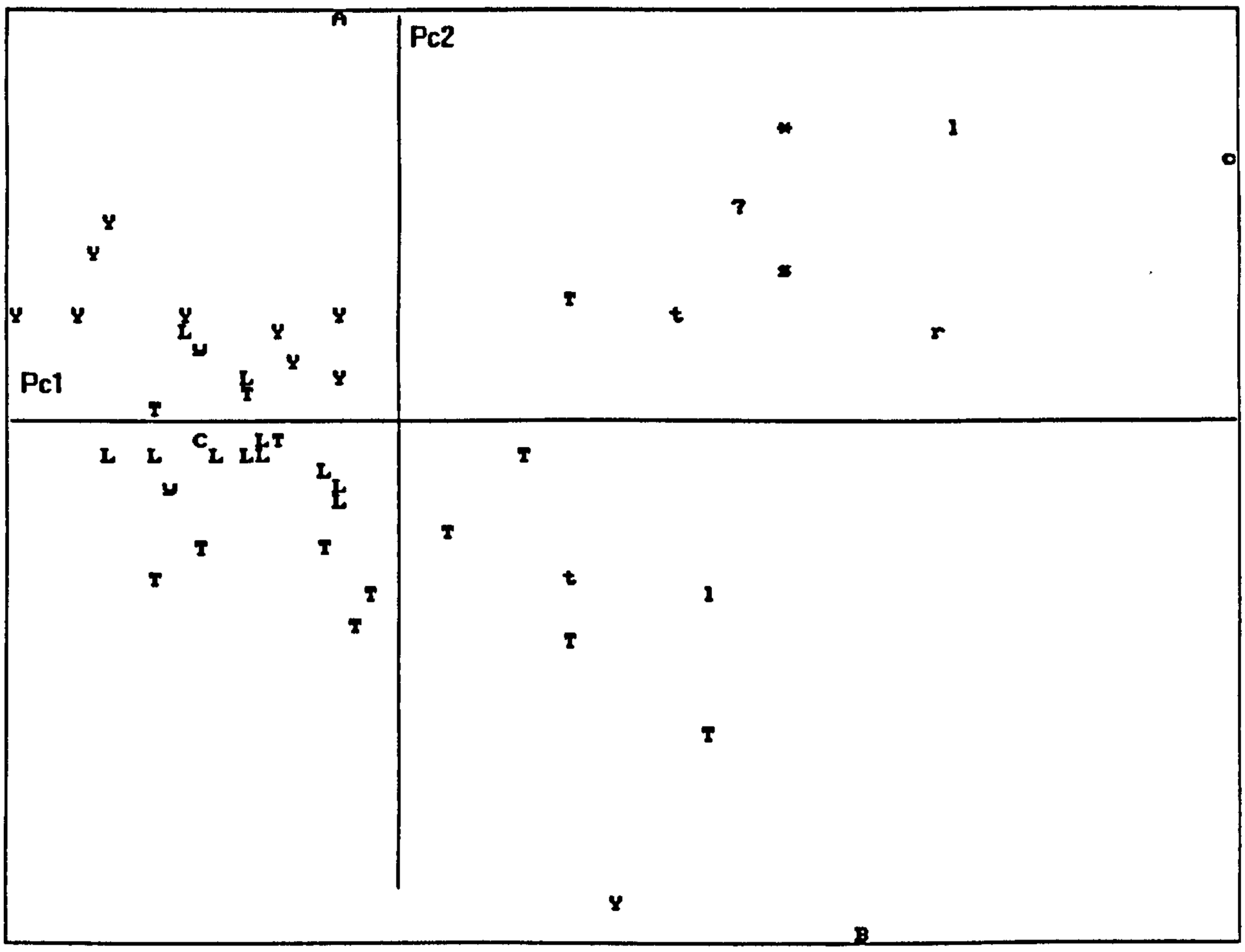


FIG.34. PCA OF TINGRITH COINS USING AS, CO AND SN.
KEY AS FIG.33.

A further investigation took the products of a particular mint, Trier, over two particular issues and analysed ten coins from each issue. The addition of this data to the PCA analysis produced the plot in Fig.35. This clearly shows that, using all elements, the products of the mint of Trier all cluster quite nicely. Indeed, it is gratifying to note that although the analyses plotted here represent four separate analytical batches conducted over nearly three years, the groupings remain firmly based on the archaeology.

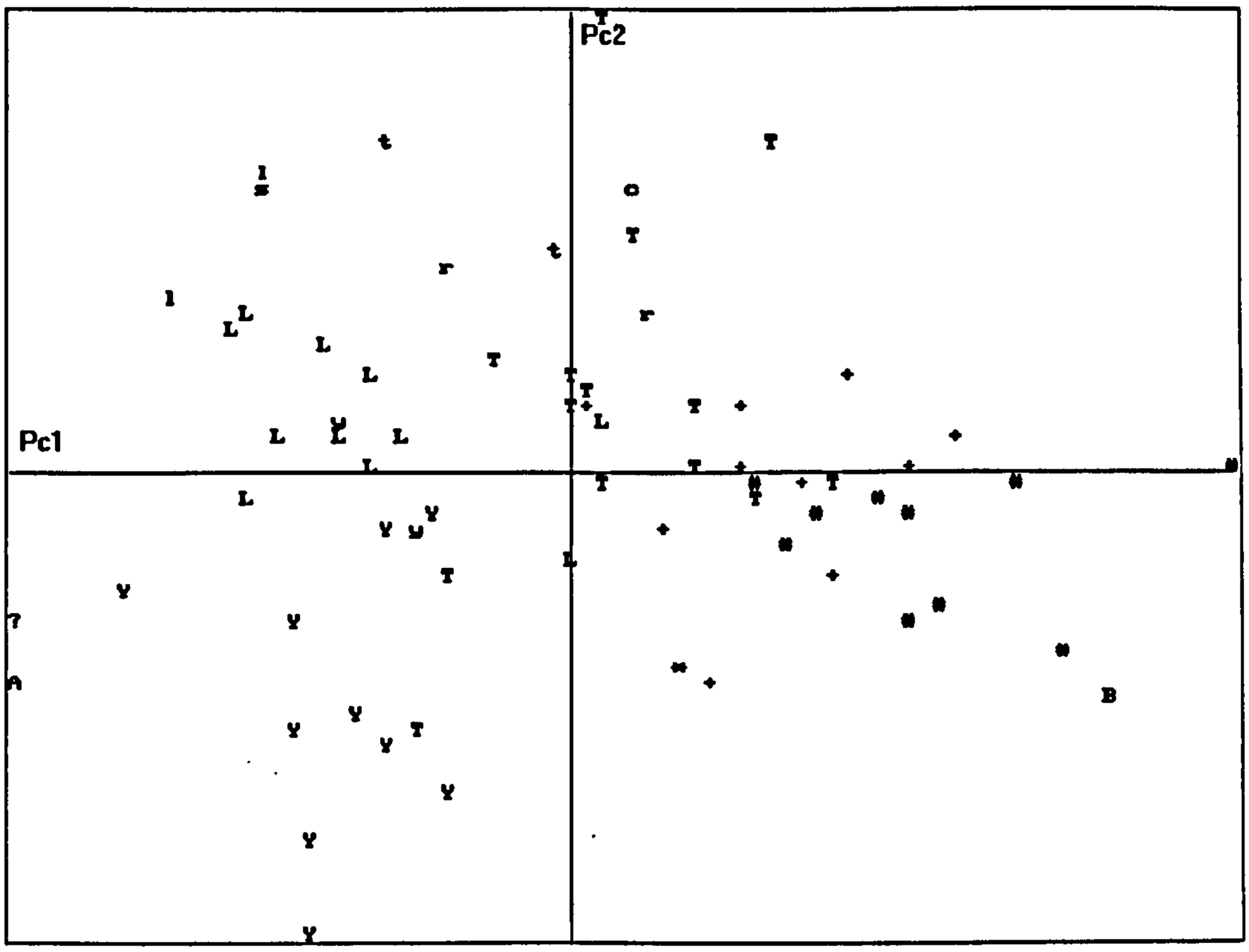


FIG.35. PCA PLOT OF ALL TINGRITH COINS USING ALL ELEMENTS.
KEY AS FIG.33. PLUS + FOR RIC 368 AND # FOR RIC 441.

This particular PCA plot also manages to pick out the 'odds' and 'as' copy candidates with better resolution than the previous all element analysis. Although they do not form a discrete group as the products of the known mints do, they do appear distinctly, and unambiguously, 'odd'. The addition of more data to the analysis obviously helps in clarifying the situation, demonstrating how small, yet real, these compositional differences are.

3.2.2.3 Discussion and conclusions

It is apparent from these analyses that the mints investigated here were, during the early fourth century, attempting to adhere to a broadly standard composition. This is especially true in regard to the silver, tin and lead contents. These are the three alloying components which would have been both controllable and worth controlling to the Roman moneyers. This is particularly apparent if one considers the degree of segregation possible during the production of this sort of complex alloy. As discussed in chapter 2, it was found in experimental work that, within a single batch of alloy, the silver content could vary by 0.5% and the lead by 4% in a comparable copper-alloy (Cope,1972.16).

The application of a variety of statistical techniques has also established that there are significant and diagnostic differences in the major alloying components between the three main

mints studied. Although patently keeping the alloys to within certain parameters, local conditions and differences in working practice, for example, lead to a small but statistically significant variability. The fact that the best clustering of the coins by issuing mint was achieved using both the major controllable elements and the trace constituents demonstrates that the groupings are dependent on both different local supplies of raw material and on differing working practice. It is obviously impossible to say anything concerning the sources of the silver, tin or lead in these coins given the likelihood of the re-melting of old issues and other sources of scrap metal. It is, however, fair to say that the trace elements present are specific to the local sources of that scrap metal, and thus enable the clear grouping of the coins on that basis.

3.2.3 The Richborough Hoard IV.

3.2.3.1 Introduction.

During the excavation of the Roman Saxon Shore fort at Richborough in Kent a small hoard of coins was found which were thoroughly corroded together. The find was published in Richard Reeces' coin report for Richborough (Reece 1968.190-1) where a date of the second quarter of the fourth century is suggested. The only visible feature on any of the exposed coins is a PROVIDENTIAE AVGG reverse type of Constantine Ist (309 - 337) which would have been issued between 324 and 325/6 (Plate 9).

Such a group of material is potentially of great interest to a project investigating the effects of post-depositional factors on copper-alloy coins. No conservation treatments had been applied to the group, which was preserved in a stable condition. Furthermore, the degree of corrosion appeared to vary quite markedly from area to area. This is of considerable interest if related to the composition of the coins in each area and the nature of the associated corrosion products.

3.2.3.2 Sampling and Analysis.

As mentioned in the general introduction, this group of material was selected specifically to study the spatial relationships of compositional variation within a group of similar copper-alloy coins. This, therefore, involved the analysis of all seventy-seven coins in the concreted hoard. This aspect of the work will be reported fully in chapter 4. However, one aspect of the analysis involved the comparison of the compositions of this material with numismatically identical coins from the Tingrith hoard, and is therefore appropriate to this section.

The assumption in most previously published reports of the compositional analyses of Roman coins is that all the variation encountered in the material is predominantly a function of the coins 'life', and not in any significant way influenced by corrosion or cleaning. This is a particularly important assumption in work where coins have been gathered from a variety of sources, as is the

case with most published analyses. Furthermore, it is usual for only the more worn or corroded examples to be 'sacrificed' to a compositional study. The resultant data are then put together and conclusions drawn concerning the variations found. These inevitably concern questions of the 'recipes' employed at different mints, and how, for example, the introduction of type 'x' saw the increase in lead content, which must have been an austerity measure because we all know that lead is cheaper than copper.

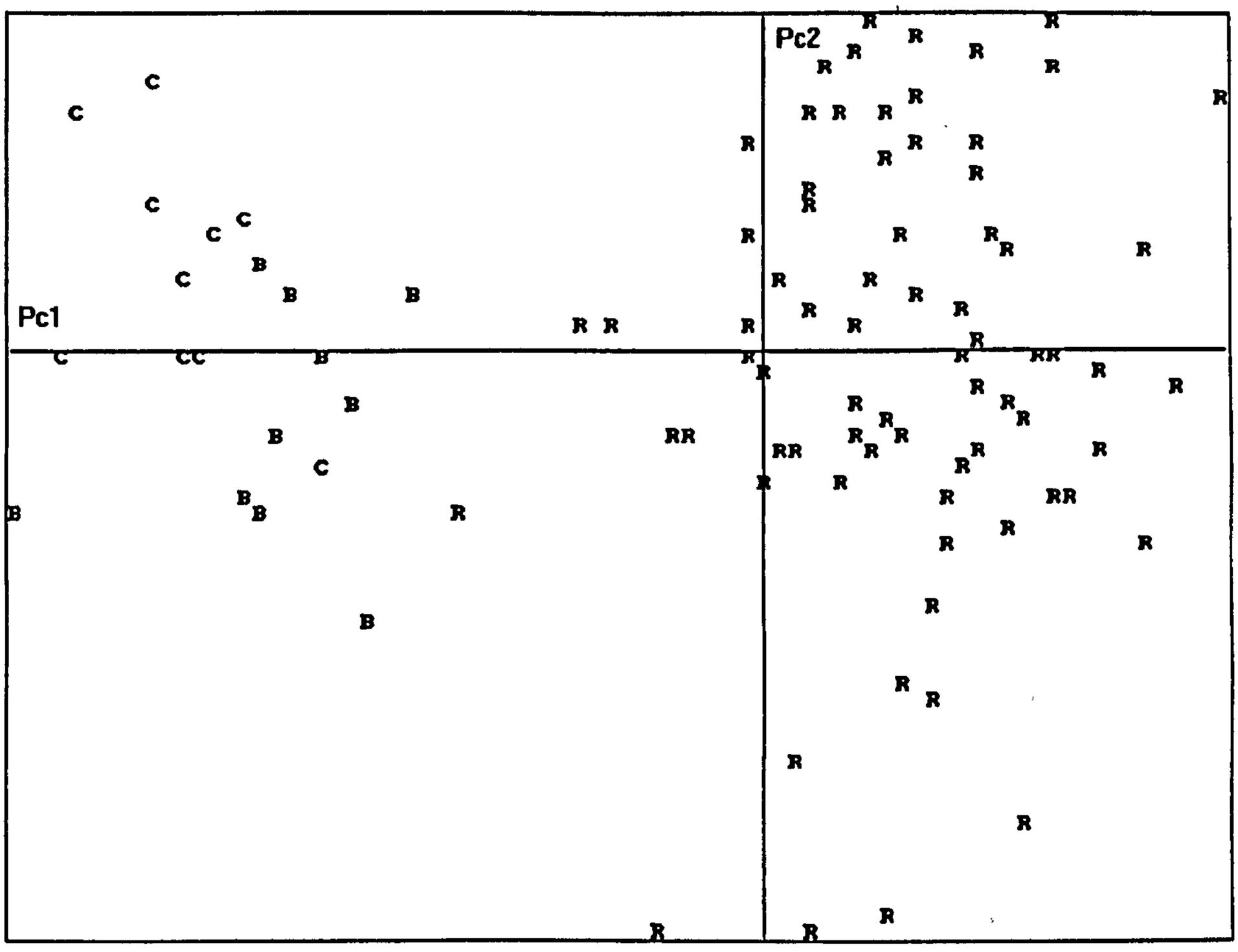


FIG.36. PCA PLOT OF RICHBOROUGH COINS AND NUMISMATICALLY IDENTICAL MATERIAL FROM THE TINGRITH HOARD.

Key: **R** Richborough coins **B** RIC368 from Tingrith **C** RIC441 from Tingrith

It was in order to test the validity of these assumptions that the twenty coins from the Tingrith hoard representing two particular issues from the mint of Trier were analysed (RIC 368 and RIC 441). These two issues of Trier are also responsible for twenty-six out of the seventy-three coins from Richborough. If the assumptions are correct, then one would expect to find no great differences between the compositions of the two groups. Indeed, it has already been demonstrated that the group of twenty Trier coins used here has a composition statistically similar to the other coins from Trier analysed, including the one comparable coin from the Bancroft villa hoard. Consequently, it was decided to run an all elements PCA on a data set consisting of all the Richborough coin analyses and the twenty coins from Tingrith (Fig.36.).

It is glaringly obvious that there are two very different compositional groups represented. The two samples from the Tingrith hoard form one discrete group, whereas all the Richborough coins are clustered together quite separately.

3.2.3.3 Discussion of Analysis.

This comparison can be interpreted only one way, and serves to illustrate that the assumptions outlined above are untrue and can have serious ramifications. It appears that the compositions of what are ostensibly numismatically similar coins are very different. Both sets of material were sampled and analysed by identical procedures and the employment of the same set of standard reference materials in both sets of analyses has ensured their analytical comparability.

The Tingrith coins came from a relatively protected burial environment and are clean and fairly free of corrosion. The Richborough coins on the other hand, were discovered as a corroded together lump, with no evidence of having been buried in a vessel of any sort. However, the coins, once freed from within the lump, are generally in quite good condition and certainly identifiable. Some even retain their 'silver' coating.

The assumption that both sets of coins should exhibit at least reasonable similarity is a numismatically tenable one. Indeed, it is born out by the work earlier in this chapter. The twenty coins from Tingrith provide an example of the degree of variation that is to be encountered within an issue. However, it is readily apparent that the difference between this group and the Richborough coins is considerably greater and cannot be accounted for by such variation.

In chapter four this aspect of the analyses will be explored more fully. However, the importance of comparing variability within groups of material which have been subjected to the same burial environment needs to be emphasised. The relevance of this type of comparison to compositional analyses of all copper-alloy artefacts is obvious, especially given the sensitivity of statistical methods to even small amounts of variability.

3.2.4 The Bancroft Villa Hoard.

3.2.4.1 General introduction

This hoard was discovered during the course of excavations at Bancroft Roman Villa (Milton Keynes) in 1978. The 76 coins were found scattered on a floor surface and not associated with any vessel. Despite this, according to the conservation report (TN2604-unpublished internal report), the majority of the coins were in very good condition, requiring only light mechanical cleaning. This would suggest a compatively benign burial environment, possibly no more aggressive than that inside the Tingrith or Walbottle vessels.

The coins are all nummii of the AD 330's, with 90% issued between AD 330 and AD 335. One of the coins was earlier, a PROVIDENTIAE CAESS issue struck between 325 and 330 at Trier, five coins were later, dating to between 335 and 341 (King 1981.41). The hoard was regarded as unusual by King (1981.41) because of the large number of coins identifiable as copies (25%). These were identified primarily on the basis of their smaller size, the quality of their manufacture being relatively good. This provided an excellent opportunity to test King's (1978) hypothesis which is based on her work on the Woodeaton hoard (see chapter 2). Kings' (1978) work suggests that the copies are compositionally significantly different from their prototypes. Their style and fabric are generally so good that it is really only possible to tell them apart by the composition of their alloy (King 1978) (Plate 10). Furthermore, in the discussion about King's work (see chapter 2), the limitations of the technique used are explored. The use of AAS to analyse a selection of numismatically identical material will enable a fuller and more reliable compositional study including the assessment of the minor and trace components.

3.2.4.2 Analysis and results

A total of twenty-two coins were randomly selected for analysis. Sixteen of these had been classified as 'official' issues by King (1981), the remaining six being classified as copies. This maintains the percentages of copies (27%) and 'official' issues (73%) in the hoard as a whole. Of the 'official' coins; nine are issues of the mint of Trier, six of Lyon and one of Arles.

The coins selected were each sampled by drilling (see chapter 2), and the resultant metal turnings were analysed by AAS. The analyses were conducted under the same conditions as those in the preceding sections, using a combination of SRMs and standard solutions to ensure the necessary high level of accuracy.

A preliminary look at the resultant data quickly divides the copies from their prototypes on the basis of their silver and lead contents (Fig 37).

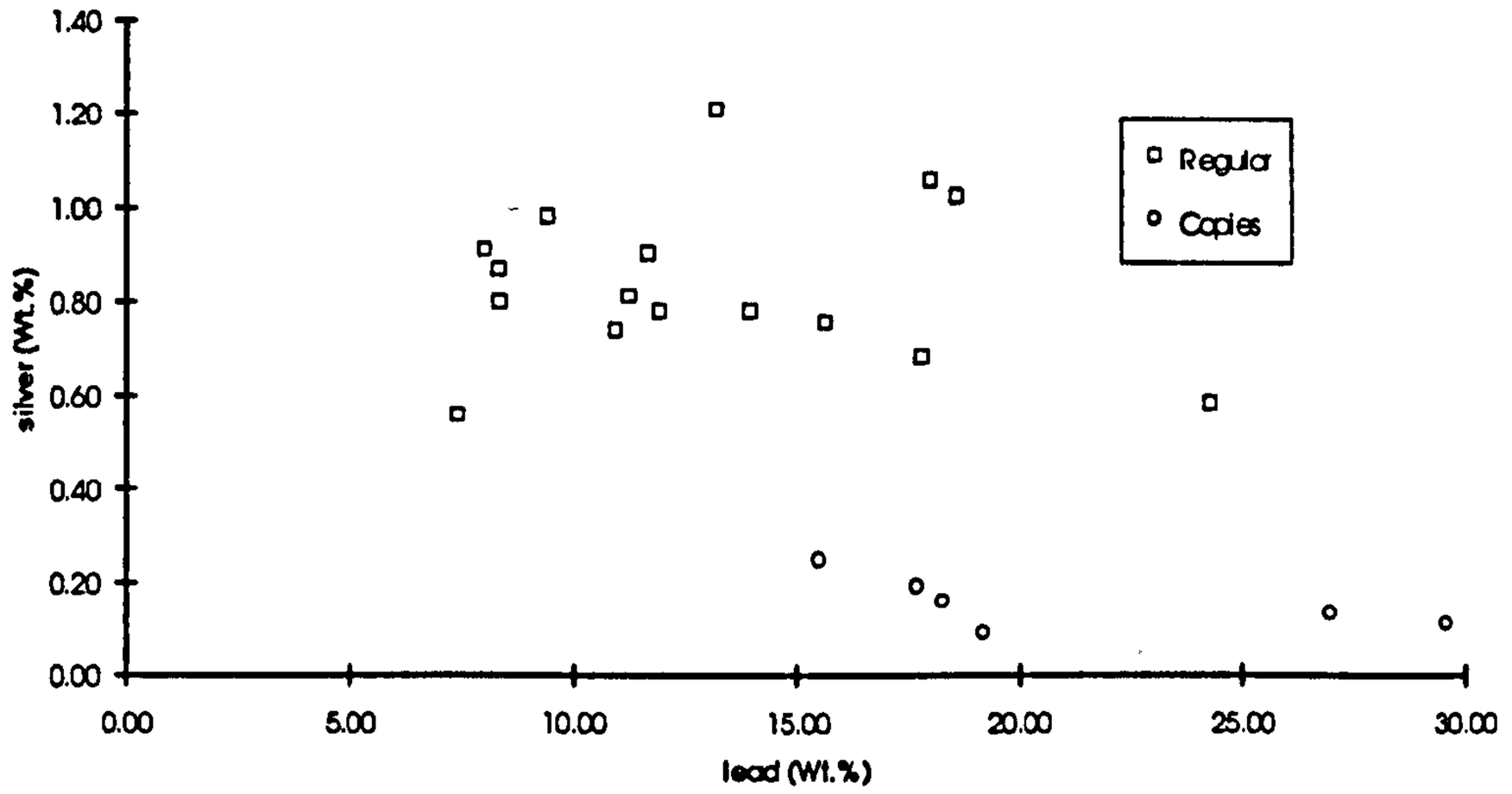


FIG 37. PLOT OF BANCROFT HOARD SILVER AND LEAD CONTENTS

A principal component analysis (PCA) of the covariance matrix was then conducted on log-transformed data in the usual fashion. Fig. 38 shows the resultant plot using all nine elements (tin, lead, silver, zinc, nickel, iron, arsenic, cobalt and chromium).

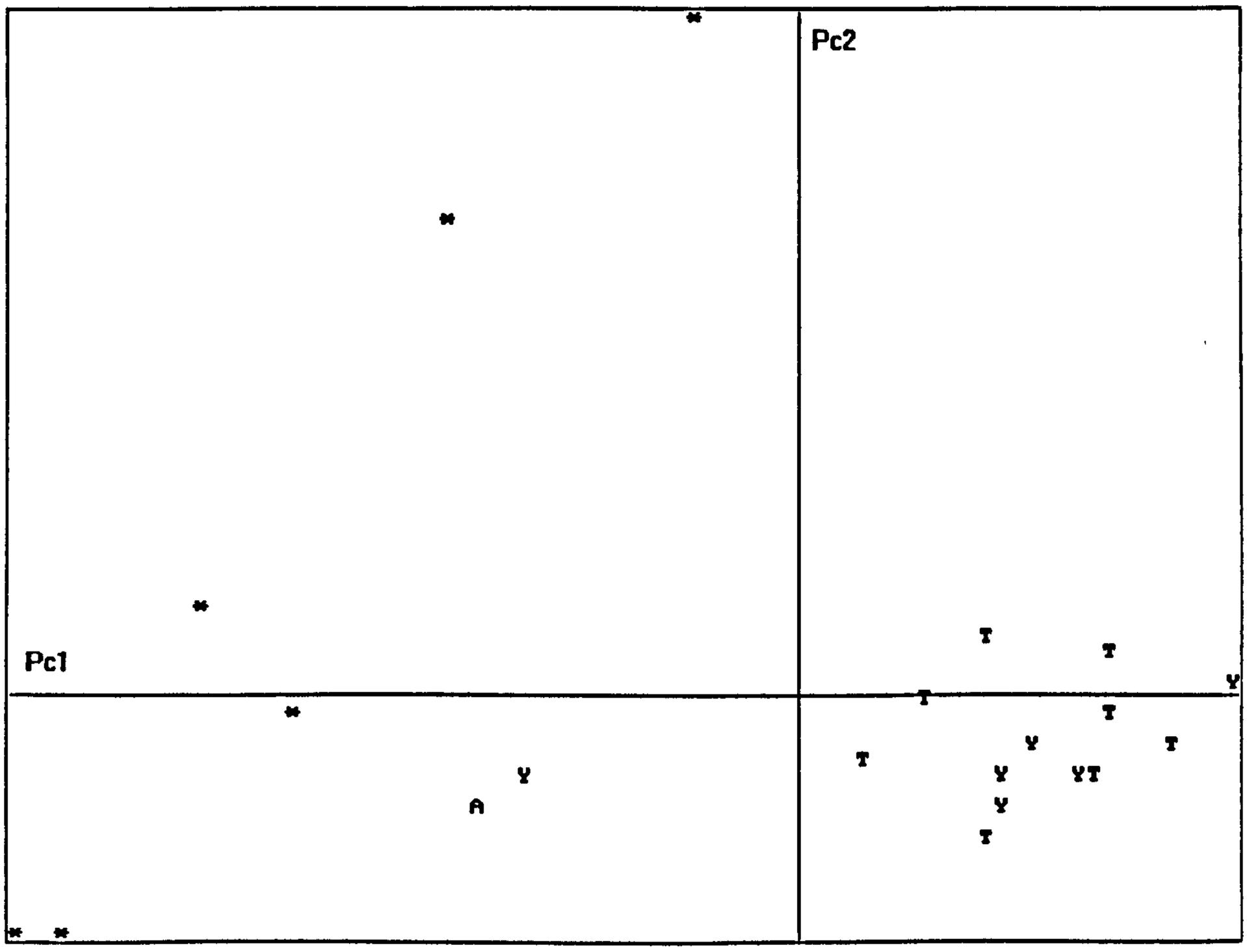


FIG 38. PCA PLOT OF BANCROFT SAMPLE, ALL ELEMENTS

T Trier Y Lyons A Arles * 'Copies'

The copies are clearly separated from the official issues but are scattered over a relatively large area. The one coin of Arles is also separated from the tight group of official issues, as is one coin ostensibly (according to mint signature) from Lyons (No.46). Dividing the data into major, controllable components (tin, lead and silver) and minor/trace impurities (zinc, nickel, iron, arsenic, cobalt and chromium) produces the same differentiation, with the exception of coin No.46. This coin, identified as 'official' by King (1981), is grouped with the copies and the single coin with an Arles mint signature by its minor/trace composition, but with the 'official' issues by its major components. This may be just one aberrant coin, yet its trace element profile is so different from its other 'official' cousins that it is very likely to be a copy. Furthermore, its silver content, although high by copy standards (0.56%) is the lowest silver content recorded for any of the 'official' issues analysed here. Consequently it is felt that re-attribution as a copy is necessary on the basis of its composition. The coin with the Arles mint signature may also be a copy, having only 0.58% silver, although, being a single example, this cannot be substantiated.

In order to try to understand the compositional differences between the 'official' issues and their copies further, a subset of those components contributing the most to these groupings was taken. These were lead, silver, zinc and iron, and the resultant plot is shown in Fig. 39.

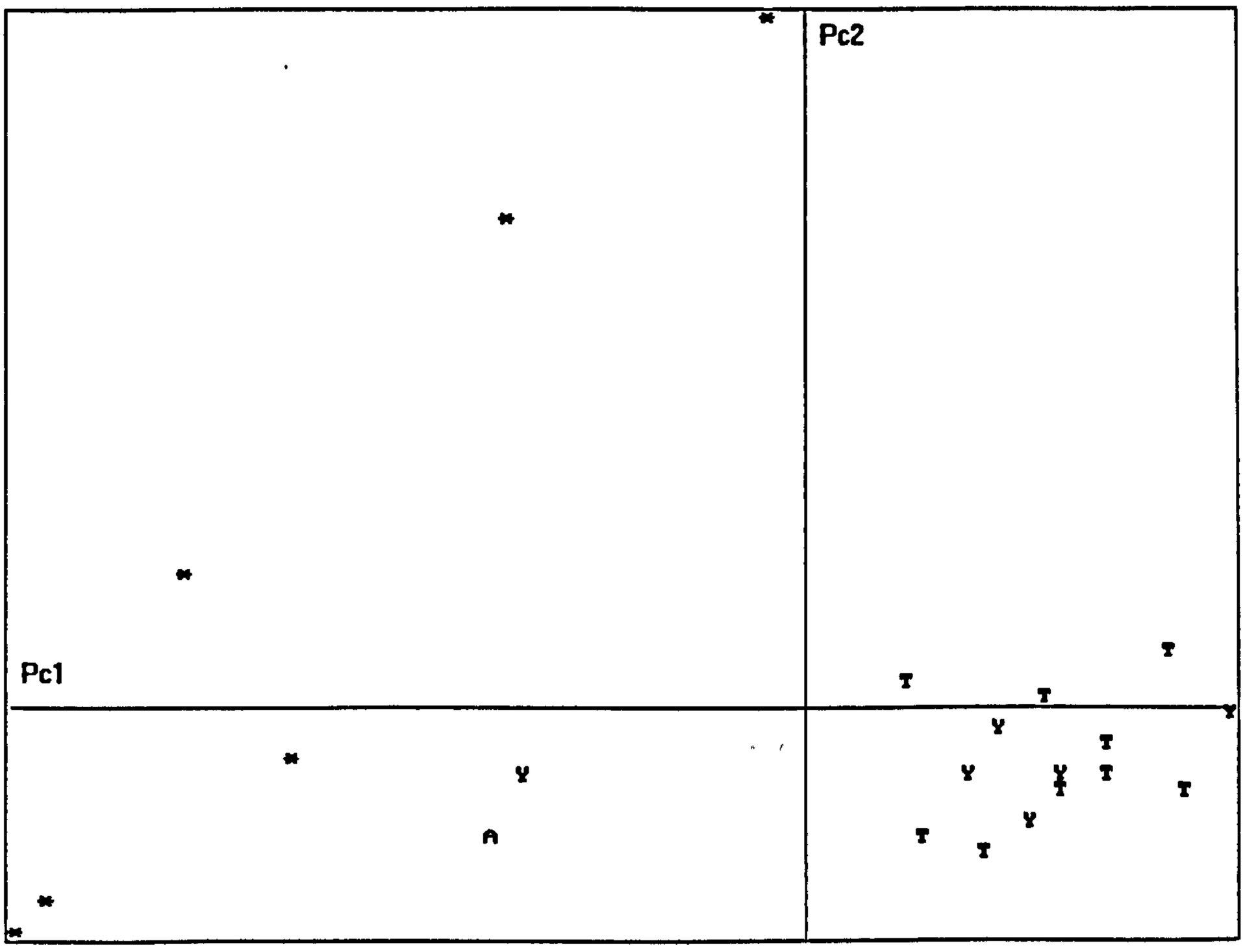


FIG. 39. PCA PLOT OF BANCROFT SAMPLE, SUBSET

This produces greater differentiation between the groups than would be expected. The 'official' issues are very tightly clustered, the copies scattered in a diffuse but distinctly different

group. The two coins which this analysis re-attributes as copies compositionally are clearly grouped with that cluster.

To substantiate the assumption that the Bancroft Villa coins were relatively un-affected by their burial the analytical data were compared with the analyses of numismatically identical coins from the Market Deeping site finds. Initially a principal component analysis was run which produced the plot in Fig 40. This clearly separates the Market Deeping coins from the Bancroft coins, both copies and 'official' issues.

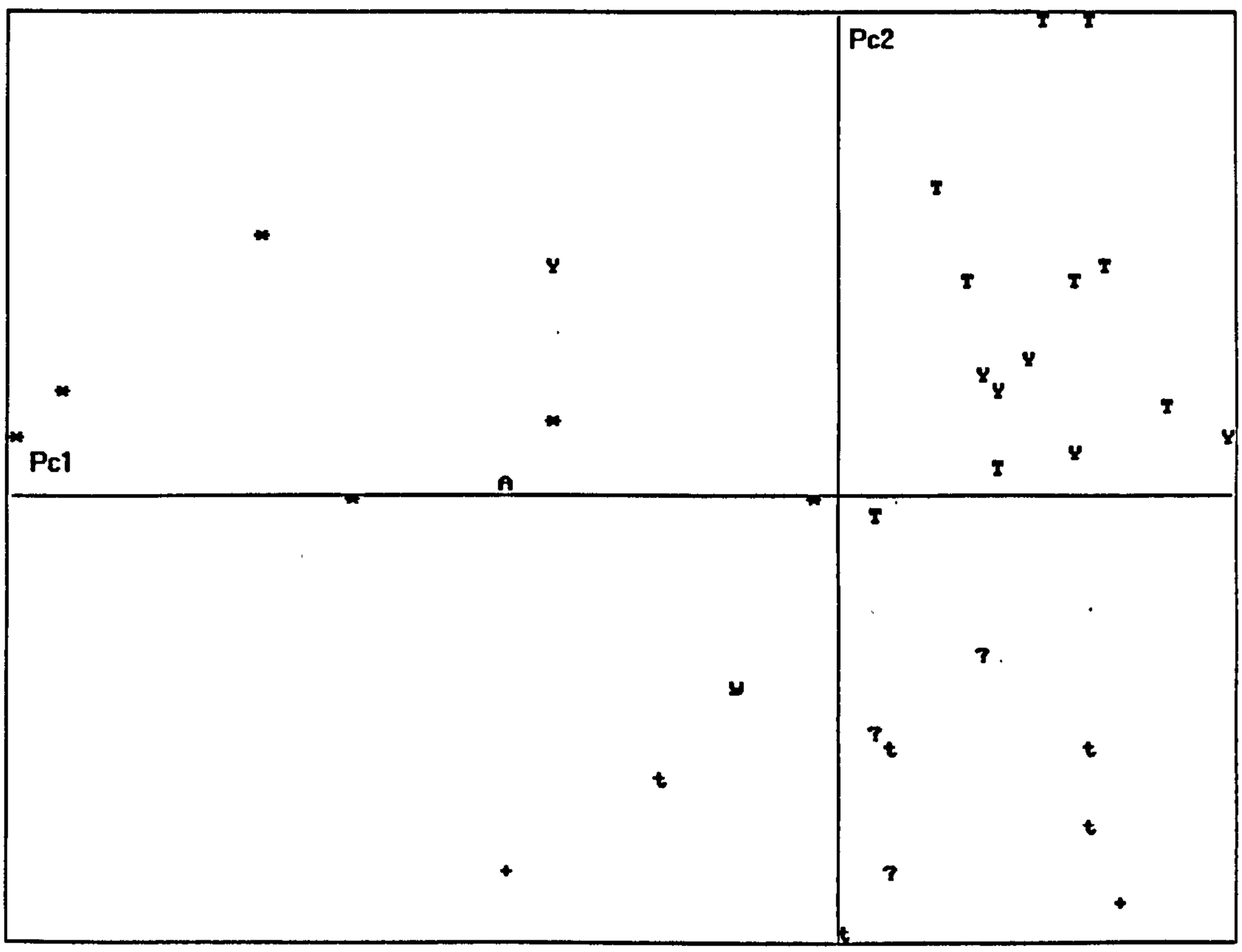


FIG. 40. PCA PLOT OF MKT.DEEPING AND BANCROFT VILLA COMPOSITIONS.

t Deeping Trier + Deeping Copies y Deeping Lyon T Bancroft Trier
Y Bancroft Lyon * Bancroft Copies

The variable loadings (table 8) show a complex interplay of constituents, with the first two components only responsible for 57% of the variation. The first component (axis) is largely describing the iron values, together with large contributions by silver and zinc. The second axis shows a general opposition between the arsenic and chromium on the one hand and the cobalt and iron on the other. The significant part played by the iron is clear. Iron is responsible for a

large part of the difference between the copies and the 'official' coins (along with silver and zinc). It is also responsible for a significant part of the difference between the Market Deeping coins and the Bancroft coins.

Element	Pc1	Pc2
Ag	53	14
As	19	46
Co	10	-59
Cr	18	56
Fe	120	-22
Ni	13	-13
Pb	-14	-3
Sn	35	-2
Zn	46	19

TABLE 8. VARIABLE LOADINGS FOR ALL ELEMENTS PCA (X100).

To try to clarify this situation a further principal component analysis was conducted using only the values for silver, nickel, lead, tin and zinc. These are elements whose significance is overshadowed by the arsenic, cobalt, chromium and iron in the first run, yet are likely to make a significant contribution given the low cumulative percentage for the first two components. The resultant plot of this analysis (Fig. 41) is interesting in that it places greater emphasis on the differences between the copies and the 'official' issues than on the differences between origin. The 'official' coins are clearly clustered together with the copies making a diffuse group of their own. The coin denoted by '+', and clustered with the 'official' coins, is regarded as a copy stylistically by the numismatist. The coins denoted by '?' are identified as 'official' nummi of the House of Constantine, but with no visible mint signatures or legends. All appear to be 'official' on the basis of this plot.

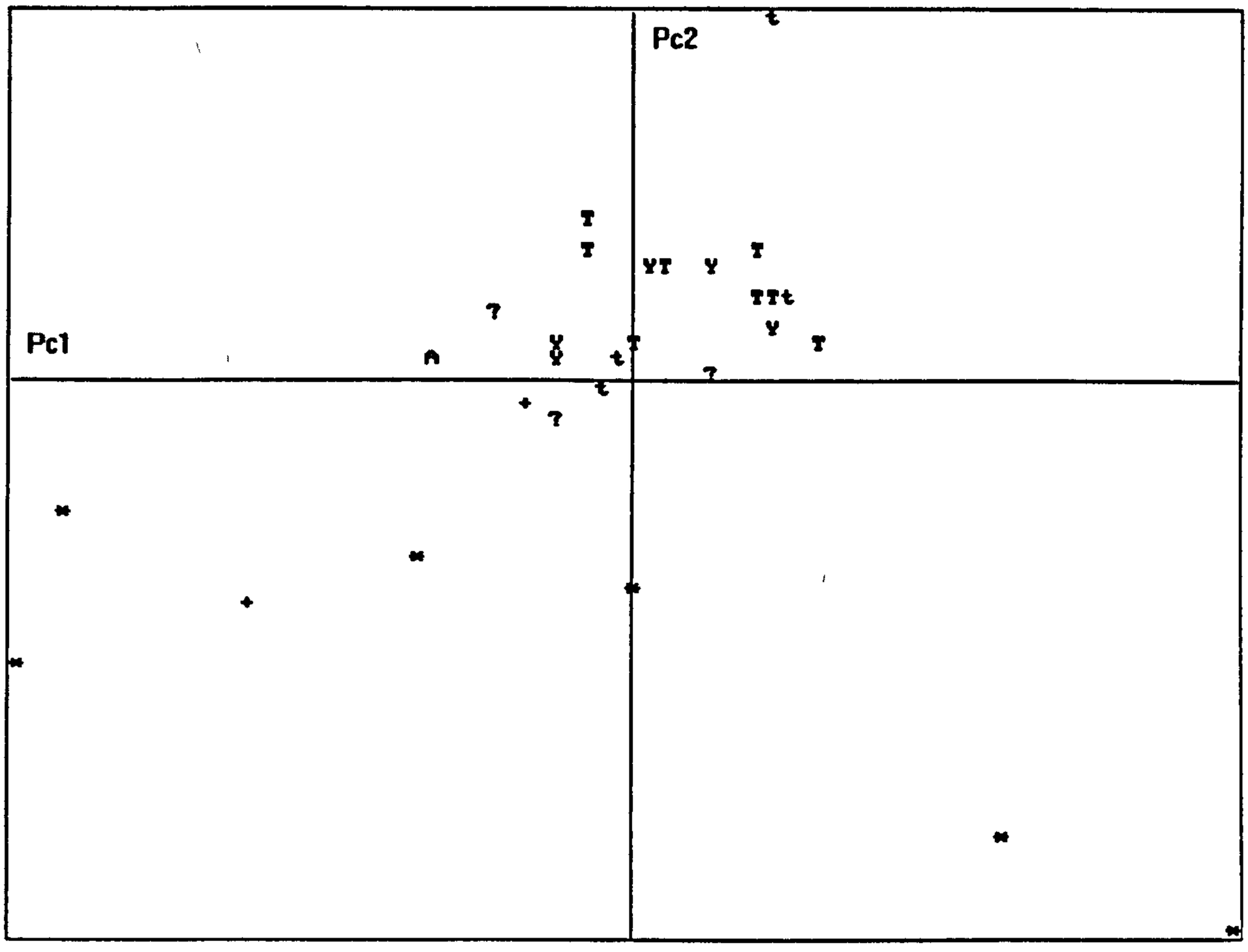


FIG. 41. PCA OF MKT.DEEPING AND BANCROFT SUBSET

(key as for previous figure)

This analysis attributes 78% of the variability to the first two components. Of these, zinc dominates the first component with the second component being shared largely by silver, lead, tin and nickel.

Element	Pc1	Pc2
Ag	17	65
Ni	12	25
Pb	-8	-19
Sn	37	23
Zn	100	-24

TABLE 9. VARIABLE LOADINGS FOR SUBSET PCA (X100).

This is in keeping with the initial findings that the copies are differentiated, in this analysis, most strongly by the controllable alloying components. The role of the zinc is interesting, being largely responsible for the spread of the copies along the first axis. It may be significant that the same spread is shown in the principal component plots of the Bancroft hoard coins only with the same general distribution. The two coins at the bottom right of the plot are both copies of the URBS ROMA type whereas the copies to the left are predominantly of the GLORIA EXERCITUS (two standards) type. Both 'official' versions were issued at the same mints over

the same period (330-335) and show no compositional differences. The fact that their copies do may be of some significance.

3.2.4.3 Discussion and conclusions

The findings of King's (1978) XRF analyses have generally been confirmed, and built upon further by this analysis. The presence or absence of silver and the amount of lead have been confirmed as diagnostic traits capable of distinguishing between copy and 'official' coin. However, the silver is not totally absent, just very low (but well above the detection limits; see appendix 2). Tin does not appear to be as diagnostic in this group as King found in the Woodeaton coins, although a larger sample would be needed to be certain.

The accuracy and sensitivity of AAS has enabled investigation of the minor and trace components. These are also useful in distinguishing between copies and 'official' coins, showing that not only were the copies *not* attempting to reproduce the 'official' coins compositionally, but that different sources of metal were employed. The differences in minor and trace elements appear so marked that it is unlikely that the copies were produced from the melted down and de-silvered 'official' coins, as has sometimes been suggested. The identification of iron and zinc as the most significant trace elements distinguishing between the two groups is interesting. The lower iron content of the copies is likely to reflect the technology used to produce the copper used by the copiers. This would suggest that the copies are produced from highly refined metal (see chapter 5 for a discussion of this). The higher zinc contents links this outbreak of copying to the 'barbarous radiates' of sixty or so years earlier (see chapter 3.1). This would appear to relate to the accepted view (Boon 1988) that the metal used by the copiers was re-cycled scrap, and not primary metal or re-cycled coins themselves produced from primary metal. Analyses of domestic metalwork from the late Roman period shows that small amounts of zinc are not uncommon (Bayley 1990; Tylecote 1986), whereas only very small trace amounts (in the order of 0.05%) are ever found in 'official' coinage alloys.

Comparison of the Bancroft Villa analyses with the analyses of the heavily corroded but numismatically similar material from Market Deeping supports the assumption that although unprotected, the Bancroft coins have been little affected internally by their burial environment. The low cumulative percentage achieved for the first two components in the first PCA suggests complex relationships between the two groups and between these and their two different environments. Iron is shown to be significant both in distinguishing between copies and 'official' coins and in distinguishing between the coins from Bancroft and the coins from Mkt.Deeping. Silver and zinc are also responsible for much of the difference between the two sites. This is not surprising given the susceptibility of the silver and zinc to corrosion effects. Furthermore, it is significant that once those elements which are responsible for the variation created by corrosion

are removed from the analysis it becomes possible to differentiate between the copies and the 'official' coins despite the differences in corrosion. The fact that this is still possible demonstrates how profound the differences between the copies and the 'official' issues are.

3.3 '*FEL. TEMP.*' copies: The Stoneykirk Hoard

3.3.1 General introduction

This section deals with the third and final period of copying addressed by this study, and the one which previously has received the least attention analytically. The material analysed for this study came from the parish of Stoneykirk in Scotland, and is here compared with similar material analysed by the Ancient Monuments Laboratory from North Leigh Villa in Norfolk (Knight 1984) and Lydney Park in Gloucestershire (Boon 1988). The main aim of this section was to investigate the compositions of both the officially produced 'FELIX TEMPORUM REPARATIO' and associated issues (FTR) and their copies (see chapter 2 for background), and how their composition is affected by corrosion. The Stoneykirk hoard material is also compared with similar issues from the Market Deeping assemblage.

3.3.2 The Stoneykirk Hoard.

3.3.2.1 Introduction

This hoard of 119 mid-fourth century copper-alloy coins was discovered on 29th October 1913 by labourers working for the local council. The find was made whilst clearing top-soil from off rock at Balgreggan Quarry in Stoneykirk parish and was found together with pieces of the ceramic vessel within which the coins had been buried (Macdonald 1913).

In the published report of the find (Macdonald 1913) it was reported that the vessel had been broken prior to discovery. Howver, the great variation in condition of the coins would suggest that the coins had remained within the vessel for most of the burial period; a more consistent degree of corrosion would be expected for material which had been evenly exposed. Only one vessel was found with the hoard and so the mouth of the vessel would have been open. Consequently, the topmost coins would have been exposed to the full action of the burial environment and therefore more heavily corroded. It was felt that a detailed analysis of a selection of these coins would be of value in studying to what extent the visible degree of corrosion relates to any significant compositional variation within a single hoard of numismatically identical material. Furthermore, the possibility of using elemental 'finger-printing' to distinguish between official 'FTR' issues and their copies and to investigate the differences is an area of study so far un-explored. This is particularly relevant considering that

this material comes from north of Hadrians wall, and is of value in understanding the relationships between the metalwork produced by local smiths from the local scrap 'catchment' area and the presence of coin hoards in an area which was, in all likelihood, not using coins as money, but as a source of metal.

The hoard consists primarily of the issues of Constantius II, Constans and Magnentius, covering the period AD 348 to AD 354, with the suggested concealment date being in or about AD 354 (Macdonald 1914.397). The most heavily represented issues are those of the usurper Magnentius, accounting for 51% of the total.

3.3.2.2 Sampling and Analysis

A representative sample of twenty coins was selected for analysis. The majority of these were issues of Magnentius (ten out of the twenty), with six or seven issues of Constantius II and three or four issues of Constans. Some of the more corroded issues were also selected which accounts for the uncertain attribution of one of the coins. These numbers also reflect the proportions of the coins issued by the three main emperors represented. Two of the coins of Magnentius were selected because, despite being of good size and weight, their crude workmanship would suggest an un/semi-official origin. All the coins selected which retained a readable mint signature are issues of the mint of Trier, except for No.9, which is from Arles.

A number of coins were selected because of their heavily corroded state, and where possible, were duplicates of coins in good condition. One coin, sample number 14, was severely cracked through one side. It was therefore decided to take a sample from both the main bulk of the coin (which was in good, clean condition) and one from within the crack in order to gauge the effects of the inter-granular corrosion associated with such a feature.

The twenty coins selected were drilled and the samples then analysed by AAS. The data were then studied using both simple descriptive and graphic techniques and then by multi variate techniques as in the previous sections. As expected, no great variation was apparent within, what is, after-all, a relatively homogeneous group of coins. The most significant variation is in the lead and silver contents. The variation in the lead contents is unsurprising given the inevitable segregation during cooling and striking, not to mention the effects of preferential corrosion. It is noteworthy that the coins giving some of the lowest lead contents are those selected because of their corroded state. This observation would, of course, fit in well with the expected behaviour of heavily leaded copper-alloys.

The silver contents are more interesting, strengthening as they do the suggestion that two of the coins selected are the products of un/semi-official mints. Both sample numbers three and five

have a silver content of almost exactly 0.5% silver, whereas the remainder of the coins analysed have silver contents of between 0.7% and 1.73% - in fact only three coins (apart from three and five) have silver contents below 0.9% (fig.42).

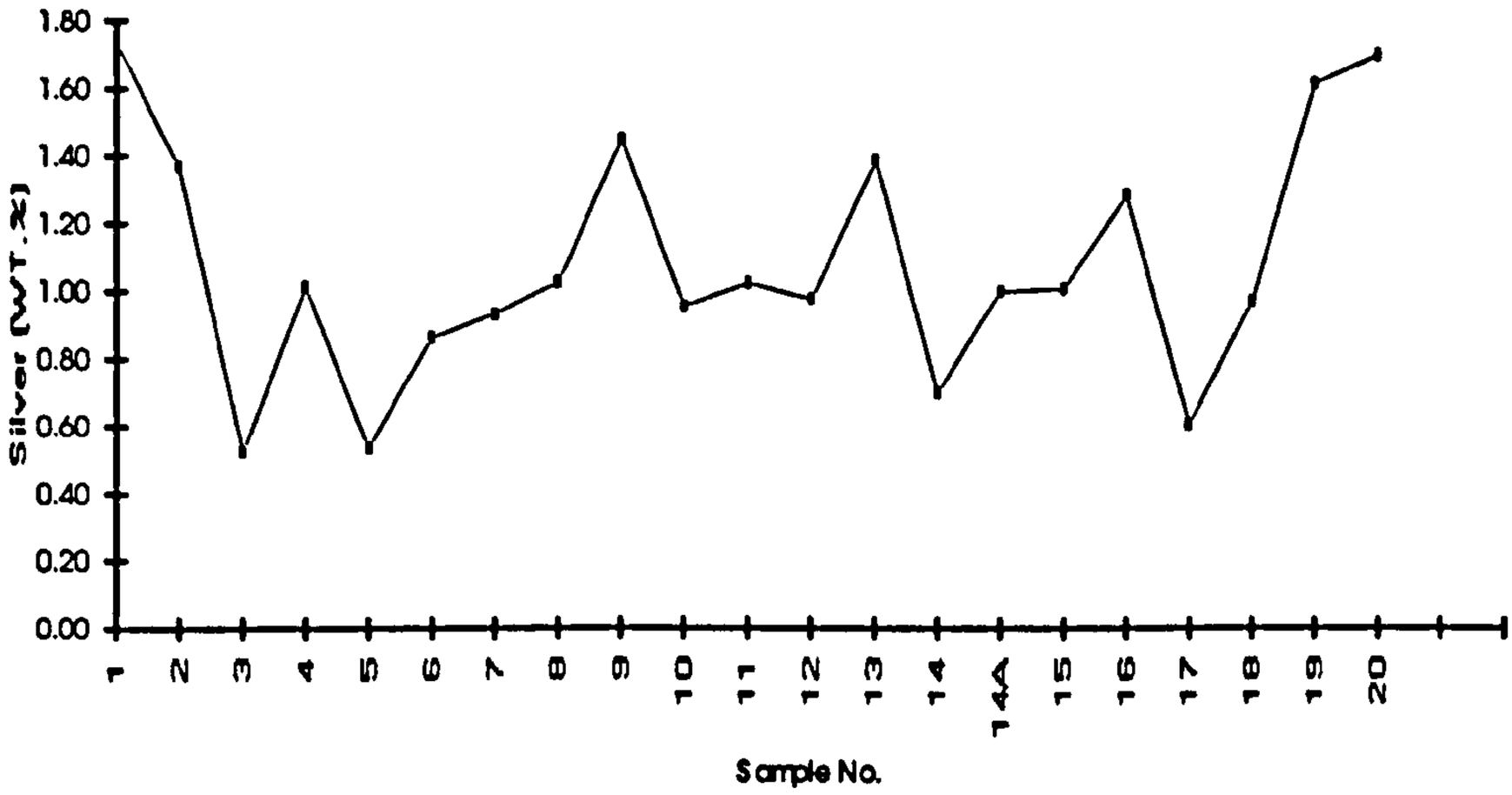


FIG.42. SILVER CONTENTS FROM STONEYKIRK HOARD SAMPLES.

It is also of interest to note that the iron and nickel contents of the two likely copies are significantly lower than the rest of the group. Once the two outliers with exceptionally high iron contents have been removed (Nos.11 and 17), the two copies with low iron and nickel are clearly separated from the bulk of the coins analysed (fig.43).

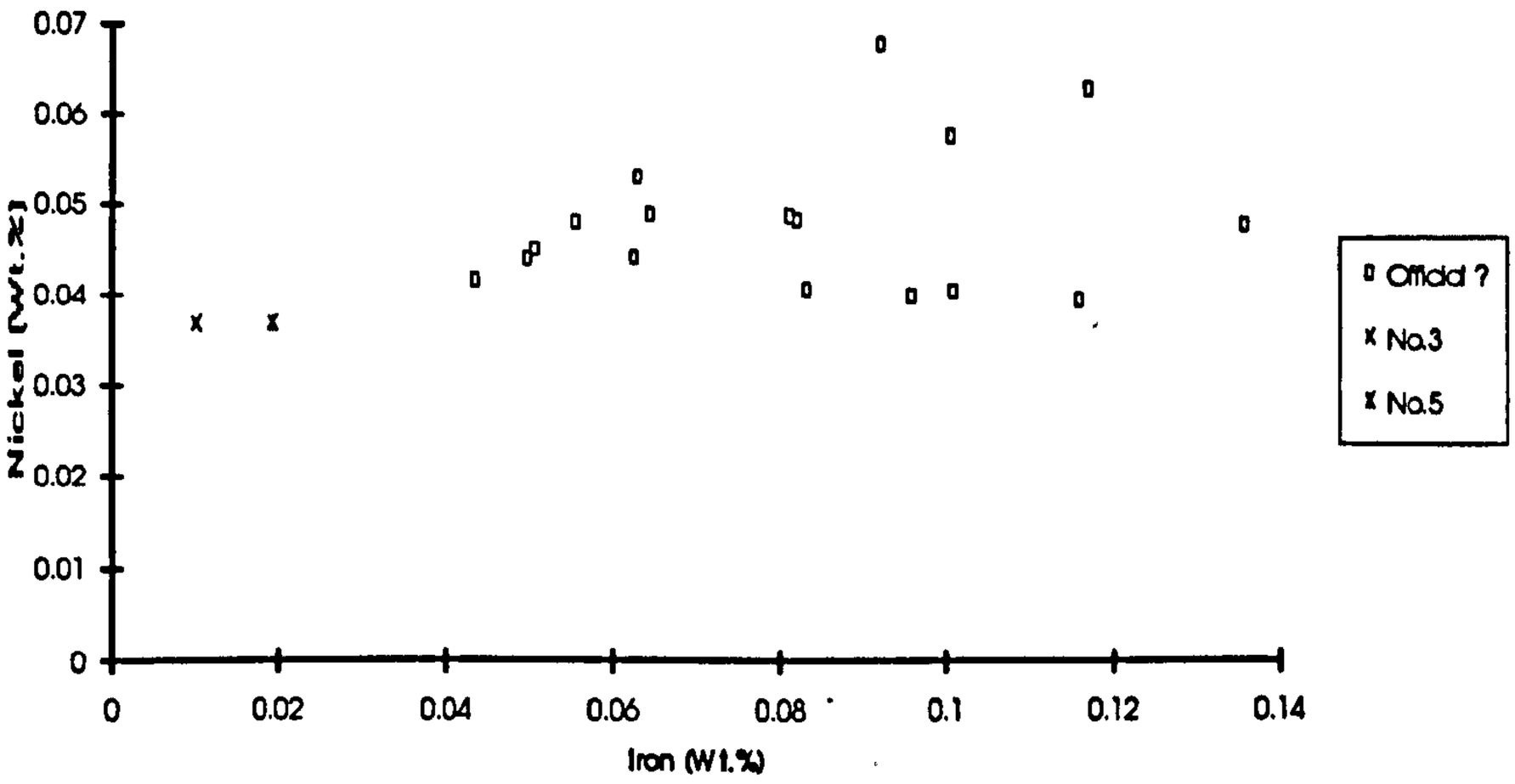


FIG.43. IRON AND NICKEL CONTENTS FOR STONEYKIRK HOARD.

Further statistical analysis was also conducted using principal component analysis in the usual fashion. A principal component analysis using all the elements which were looked for in the analysis (excluding copper) produced the plot in fig.44. This clearly separates the two copies along the first axis (PC1). The major contributors to this axis are, unsurprisingly, silver and iron (loadings of .30 and .74 respectively). Furthermore, the coins marked by the '#' sign are those selected for their highly corroded state. Three out of the four of these are separated from the main cluster along the second axis (PC2). Most of the elements detected make significant contributions to this component, however, it is interesting that iron and lead (.34 and .57 respectively) are the main elements represented.

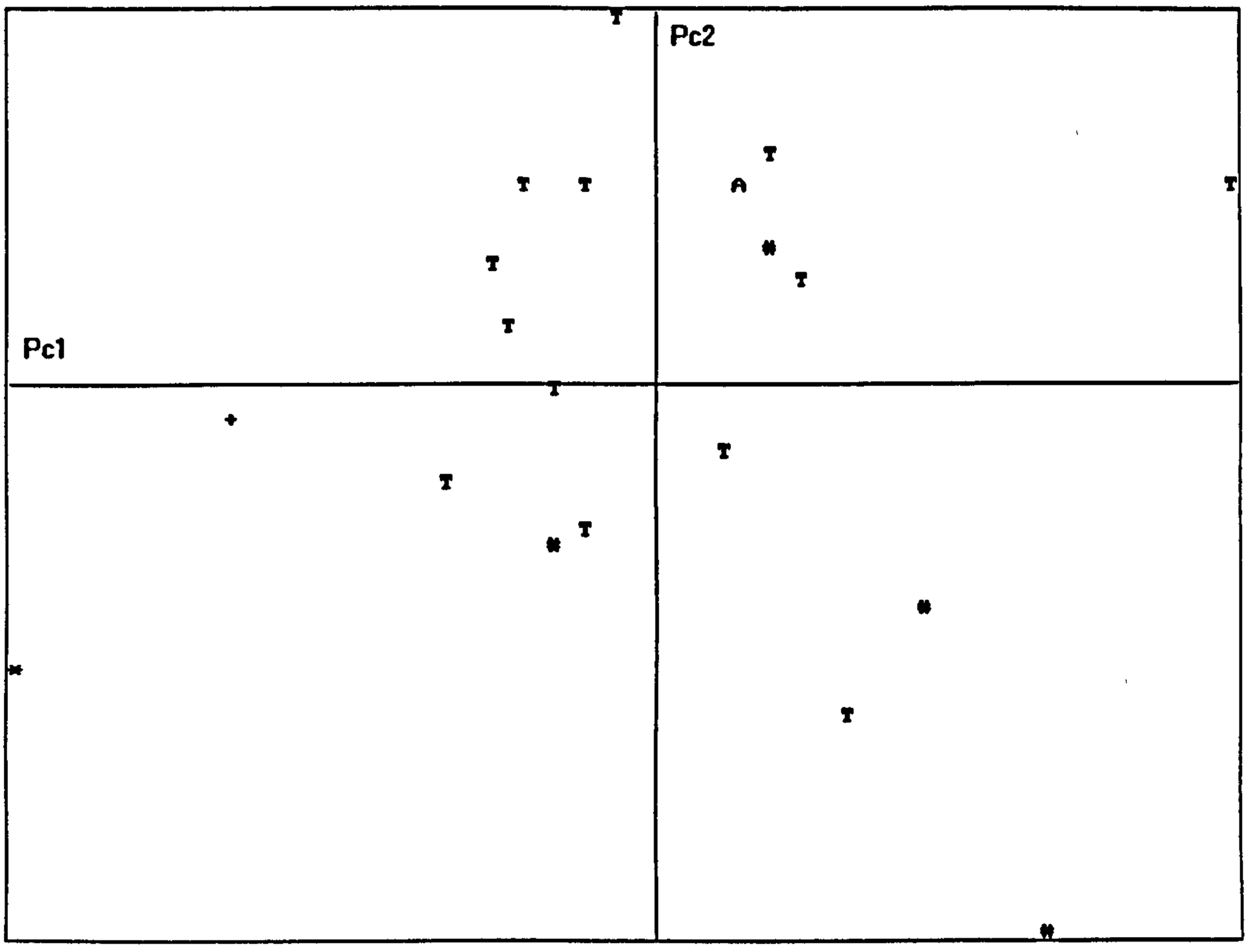


FIG.44. PCA PLOT OF THE STONEYKIRK HOARD MATERIAL USING ALL ELEMENTS.

T mint of Trier * No.3 + No.5 A mint of Arles # corroded

If we refer back to the raw data again, we see that the coins which appear more corroded and which are pulled out as being compositionally different (Nos.12, 13 and 16) are not notably higher in iron than any of the remainder. However, if we look at the lead contents we see that they are generally lower in lead. Number 12 in particular has a very low lead content together with an unremarkable iron content. Where the groups suggested by the PCA relate to archaeological or numismatic criteria it is important to appreciate that the groups are the result of a combination of data trends. Thus it is the combination of the lead and iron contents, plus the

other elements used in the analysis, which separate the more corroded coins from the bulk of the group. It is also interesting to note that three other coins are broadly within the area of the corroded coins. This would suggest that these coins are chemically more corroded than their external appearance would indicate. Unfortunately, it was not possible to confirm this by metallographic section.

The reasons for these two elements in particular to be affected by corrosion is fairly straightforward, and are phenomena already touched upon earlier (chapter 2). The iron content is liable to be increased by the inward percolation of iron from the surrounding soil (and/or associated iron artifacts), and the lead is preferentially corroded out of the copper-rich matrix.

The analysis of the sample taken from the crack in coin No.14 compares very favourably with the main sample from No.14. The compositional differences which are significant include the silver, lead and iron contents. Again, these are the elements which are most likely to be affected. The silver content is increased from 0.70% to 1.00%, the lead increases from 9.92% to 14.34% and the iron increases from 0.051% to 0.081%. The silver content could be enriched by the preferential removal of copper from the area, and the iron would be increased by the inward percolation of iron from the surrounding environment. The lead should be depleted in preference to the copper, however the analysis does not reflect this. A possible explanation of this would be if the drilled sample had included a lead rich inclusion. This occurrence is quite common in highly leaded alloys due to the mutual insolubility of lead and copper (for an explanation of the microstructure in highly leaded coins see chapter 4). However, no metallographic sections were permitted.

To take this study further the data from the FTR issues in the Market Deeping group of site finds were added and another PCA analysis conducted (Fig.45).

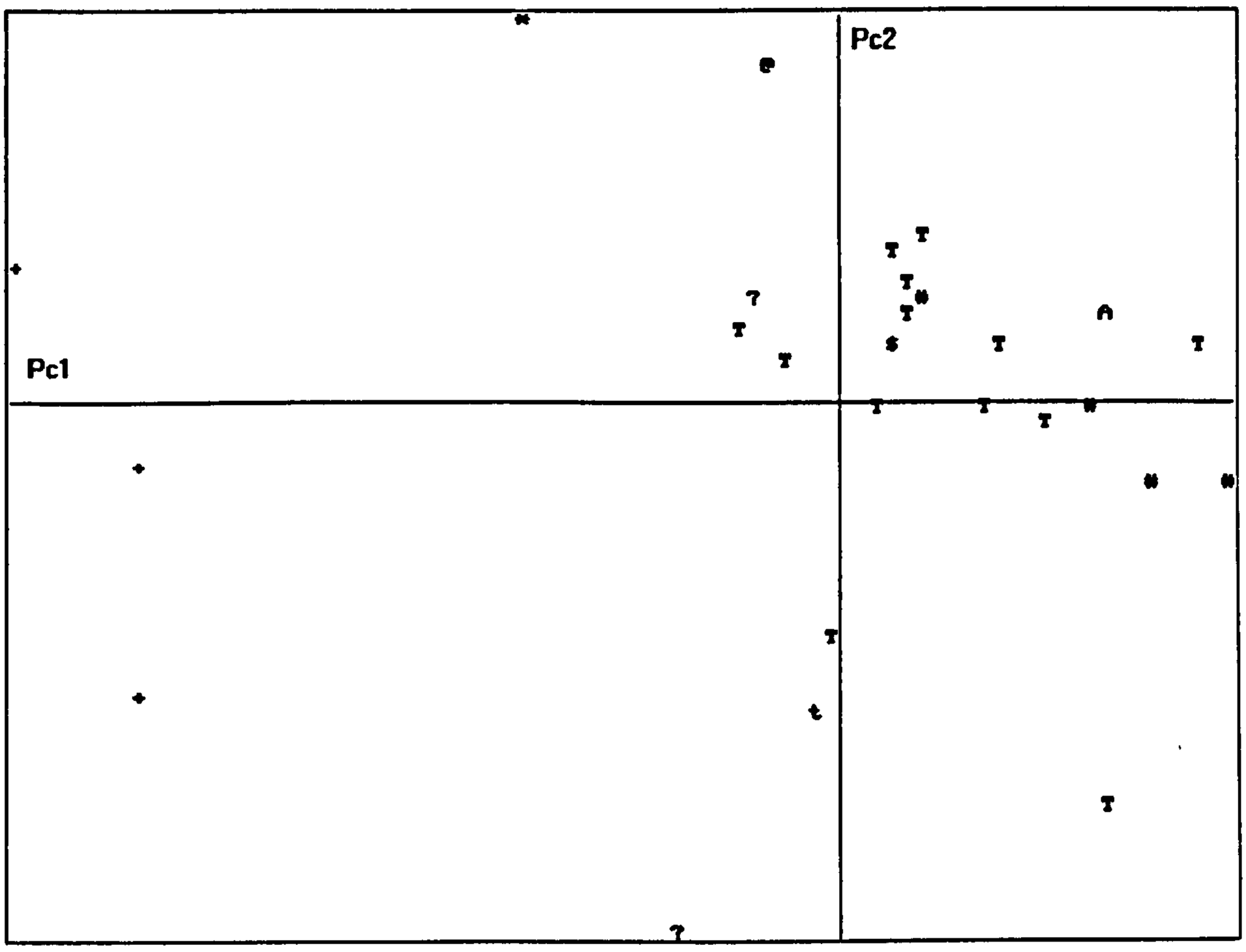


FIG.45. PCA PLOT OF STONEYKIRK AND MARKET DEEPING FTR ISSUES

+ Mkt.Deeping FTR copies * Stoneykirk No.3 @ Stoneykirk No.5

? Mkt.Deeping unknown FTR's t Mkt.Deeping Trier FTR's

T Stoneykirk Trier FTR's # Stoneykirk corroded FTR's A Stoneykirk Arles FTR

The structure picked out of this enlarged data set confirms and clarifies the picture suggested by the Stoneykirk data alone. The known copies from both assemblages are clearly separated from the official FTR coins, furthermore the Stoneykirk copies are distinct from the Market Deeping copies. This is interpreted as both an effect of differences in the burial environment and differences in the metals used.

It is interesting that only one of the Market Deeping 'official' FTR coins is grouped with the bulk of the Stoneykirk material. It is, perhaps, significant that this coin is an issue of Magnentius (presumably of Trier by virtue of its compositional attribution), although its attribution to the Stoneykirk group is more likely to reflect its level of corrosion than anything else. Indeed, its visual aspect would suggest that it has suffered less from the ravages of this sites environment than most of its fellows. The remaining two coins from Market Deeping which are regarded by the numismatist as being 'official' are grouped with the two Stoneykirk coins having the highest iron contents (Nos.11 and 17). The three Market Deeping coins stylistically identified as copies are clustered very distinctly from both sets of 'official' coins as well as from the Stoneykirk

copies. However, this distinction appears to be mainly due to the iron and nickel contents (the Stoneykirk copies being notably low in iron and nickel). If this factor is ignored then both sets of copies become more merged and distinguished from the 'official' FTR issues by the increased lead content and reduced silver content. Thus it seems that in both the case of the copies and the 'official' issues it is predominantly the iron content which is separating the Market Deeping site finds from their Stoneykirk hoard cousins.

3.3.2.3 Discussion and conclusions

This section of twenty analyses has added significantly to the few compositional analyses conducted on this class of coin by Cope and Billingham (1967) and Ravetz (1963). Furthermore it has provided a larger body of adequately comparable data from which to extrapolate the broad standards to which the copper-alloy coins of this issue were expected to adhere. The trends in the composition of the 'official' FTR issues from western mints have largely been confirmed, as have the limitations of the analytical techniques previously employed. In particular both previous analyses have taken small numbers of coins from a very disparate collection of mints in order to establish a very broad and general idea of the compositional parameters. Furthermore, although Ravetz was aware that NAA produces silver concentrations which are erroneously high (Ravetz 1963.47), her results are still quoted in numismatic literature as being entirely correct (Depeyrot 1982, for example). The current set of analyses provides a firmer basis for discussion of the compositional standards employed at the mint of Trier across a limited number of FTR issues and between the legitimate rulers of the house of Constantine and the usurper Magnentius (see chapter 5).

Ravetz (1963) published silver contents by neutron activation analysis (NAA)of whole coins for three Trier issues with the Emperor on Galley reverse type. The results are 3.5%, 3.2% and 2.7% respectively and have been used to suggest that the introduction of these coins in AD 348 marked a considerable raising of intrinsic value from the ≡1% of the previous issue (Haley 1989.106). Furthermore, because the hoarding patterns indicate a cut-off point with the introduction of this issue, it is suggested that the previous issues had become 'un-popular' in circulation because of their lower silver content (which, it is assumed was published by the authorities). The AAS analyses of five 'Galley' issues from Stoneykirk give silver values of 1.03%, 0.61%, 0.97%, 1.62% and 1.70%. These are considerable lower than those of Ravetz (1963), and do little more than suggest a continuation of the ≡1% silver standard. The silver values she publishes for later issues (Hut and Fallen horseman reverse types) are lower and generally only ≡0.5% higher than the AAS, unfortunately no direct comparison can be drawn from these issues as none are from the mint of Trier.

The reason for this discrepancy is easy to suggest. The nature of Ravetz's analytical technique (NAA) means that the whole coin is analysed including the silver enriched surface layers. This is further complicated by the fact that these coins would have been silver coated when new and this, even if worn off over time will usually leave a further enriched layer. The AAS, on the other hand, only analyses a sample taken from the 'heart-metal', within the core of the coin, which still retains the characteristics of the alloy produced at the mint.

Of particular importance to this study is the relationship between the FTR copies and their prototypes. In the only major numismatic and archaeological study of this coinage, Brickstock (1987) refers to the fact that very few analyses had been carried out, and these were of inconsistent reliability being the result of a variety of techniques over a long period. The only real conclusion that he was able to arrive at was that the copies analysed had been struck from a less-silvered, highly leaded copper-alloy. This general conclusion is supported by this analysis. Furthermore, Ravetz's (1963) NAA of the silver content of six FTR copies suggest that some of the copies have a silver content not too much lower than their prototypes. On the basis of this information she suggests that,

> "...profit lay in producing the type itself, without necessarily depriving it of silver." (Ravetz 1963.54)

This suggestion is supported by material from Ham Hill, Somerset, where an 'official' coin of Magnentius was found which had blanks for copies cut from it (Boon 1988.145). The silver content of the Stoneykirk copies would also suggest either a purposeful addition of silver or the re-use of the pre-reform coinage alloy.

Analyses of the issue immediately preceding the AD 348 reform by Ravetz (1963) gives silver contents of between 0.5% and 1.0%. Allowing for a slight over-estimation due to the technique we arrive at a figure consistent with that of the FTR copies. This would support the suggestion that the pre-reform coins were re-cycled as FTR copies, probably after the *pecuniae vetitae* edict of 356 which de-monetised all previous copper-alloy coins (Boon 1988.139). This represents a notably different attitude to the copies by those producing them, and, presumably by the population using them. In particular, it is significant that the previous spate of copying involved the reproduction of argentiferous-copper coins in an almost silverless alloy (< 0.2%). Here we seem to have a situation where a (presumably) large volume of coin in circulation was made worthless by the state and the higher value coins which replaced it were in short supply (given the relative scarcity of 'official' FTR issues on sites) (Boon 1988.140). The effect of this was to have the now useless issues re-coined as copies of the new 'official' coins without the removal of the silver.

However, the analyses of the two probable copies from Stoneykirk would suggest that the alloy used differed from that of 'official' FTR issues in a number of important ways. Obviously the

silver content is the most apparent, and one which would have been controllable by the moneyers concerned. However, the fact that the iron and nickel contents are sufficiently different from the 'official' coins would suggest that a fresh alloy was being produced. The nickel and iron would not have been controllable by the moneyers producing the copies, since they occur as mere traces. They do, however, relate to the source of the copper used and the technology used in its production. If these coins had been produced from re-cycled pre-reform coins we should expect the trace elements associated with the copper to be consistent with that of the 'official' coins. This is not the case with the two Stoneykirk copies. Although not great, the differences are sufficient to mark the coins as different solely by virtue of both their nickel and iron contents. If this suggestion proved to be correct, then we come up against the presence of the 0.5% silver, an amount which must have been intentionally added to this fresh alloy. As with the 'barbarous radiates' of a century earlier, it is beginning to appear as if there is a greater degree of organisation and control surrounding the production of at least some of these copies. This aspect of the work will be discussed more fully in chapter five.

A more comprehensive analysis of FTR copies than that of Ravetz (1963) was conducted on a hoard from the Roman villa at North Leigh, Oxfordshire, but remains unpublished. The results of this analysis form the basis of an Ancient Monuments laboratory report (Knight 1984) which compares the AAS analysis of a single FTR copy from each of the North Leigh and Lydney Park hoards, as well as looking at aspects of their production. To quote, the analyses simply give a result of, "...approximately 70% copper, 25% lead, 3% tin, traces of silver and antimony but no zinc or iron." (Knight 1984. 2). The Lydney copy, on the other hand, are reported to have given, "...greater than 97% copper, 2% lead, less than 1% tin, a trace of iron and no zinc." (Knight 1984.2). The analyses of the two likely copies in the Stoneykirk hoard are closer to the North Leigh material with 74% copper, 16% lead, 1.5% tin, 0.5% silver, 0.1% antimony, 0.02% iron and 0.01% zinc, the FTR copies from the Market Deeping assemblage are different from both; giving a mean analysis of 30% lead, 0.7% tin, 0.3% silver, 0.16% iron and 0.02% zinc. However, the totals are all very low, resulting mainly from copper values averaging less than 60%. This is interpreted as result of the aggressive nature of the burial environment encountered at Market Deeping, and must lead to questionable absolute values for all elements present. It is significant that both the North Leigh and the Lydney copies contain little or no silver[5] suggesting that some of the copies were indeed produced from a de-silvered alloy. The size and general appearance of the copies also differs significantly. The Stoneykirk copies are of the correct size and weight, with only the style and quality of the workmanship giving rise to suspicion. The North Leigh copies, in contrast, are notably smaller (average of 9mm diameter) than the 'official' coins (22mm) and of cruder workmanship. The Lydney copies could be even smaller with 1,241 out of a total number of 1,646 pieces being under 7.5mm (Boon 1988.142). It seems, therefore,

[5] The silver content of a piece of cut rod used for coin manufacture from North Leigh analysed by E/D-XRF at the BM research labs was 0.104% (Cowell. pers comm).

that there were at least two levels to this episode of copying; maybe an initial phase of large copies struck on re-cycled pre-reform metal or a specially prepared alloy closely copying the pre-reform recipe, followed by the larger scale production of smaller, cruder copies in de-silvered metal. This topic will be discussed further in chapter five.

The significant effect of the degree of corrosion which this particular section has investigated is of particular interest. As this is a largely homogeneous group numismatically speaking, it has enabled the compositional differences engendered by corrosion to be more clearly identified. The demonstration of the potential error in using variously corroded (or indeed chemically stripped) coins for analytical work of this nature must force a re-assessment of much of the data currently used by numismatists in the writing of Late Roman economic history. Furthermore, the use of small data sets of material unsuitable for comparison, and the uncritical acceptance of data (despite the authors own criticisms) has been shown to create a false interpretation of the archaeological evidence.

3.4 The Market Deeping site finds.

3.4.1 Introduction

This group of material was selected as a compositional contrast with the other hoard material analysed. The group also covers all three periods under investigation in this thesis and supplied both official issues and their copies. The coins come from a recently excavated but unpublished site in the Fens and have received no conservation treatment other than slight mechanical cleaning (Tribe. pers. comm.). All the information included here is taken from the Fenland Management Project research design supplied by courtesy of the area conservator, Adrian Tribe. The acidic, peaty soils of the area have attacked the metal of the coins severely, causing many of the coins to be un-identifiable by the numismatist (Dr. John Davies) except in the broadest terms. The coins chosen for analysis were the better preserved examples, some well enough preserved to allow exact attribution to both mint and issue.

The site (MAD 2) was initially identified during field survey conducted as part of the Fenland Project and was excavated by Lincolnshire Heritage Trust in 1991. The excavation was the first to investigate a fen-edge Roman site, and was aimed at clarifying the confusing evidence for the Iron Age/Roman transition. The project revealed both Iron Age and Roman settlement; a Romano-British enclosure over-laying what appeared to be an Iron Age salt production site. The site is situated on a clay ridge by the course of a shallow prehistoric stream. The over-laying stratigraphy is waterlogged, some areas containing much waterlogged timber in situ.

3.4.2 Analysis and results.

A total of twenty-eight representative coins were selected for AAS analysis, covering each of the three periods of endemic copying investigated in this study. The better preserved examples were selected in order to allow as accurate an attribution as possible. This was particularly important because the main use of these data was to be compared with numismatically similar coins from the hoards. The direct comparisons with the hoard material has already been dealt with in the appropriate sections above.

Within the group as a whole five subjective corrosion levels were defined ranging from 'slight corrosion' through to 'mineralised'. A discriminant analysis, aimed at testing these attributions, gave 75% correctly attributed on the basis of their composition. Where there is disagreement between the statistical attribution and the visual attribution it is usually merely a matter of moving the coin from the 'slightly corroded' group to the 'corroded' group. Consequently a 75% agreement with such a subjective set of criteria can be regarded as significant.

Comparing the mean values for each element for each corrosion group (table 10) also yields results. The 'mineralised' group is notable for the lowest copper values and the lowest totals (sum of all elements together). The lead contents also become progressively lower the greater the degree of corrosion. This is what would be expected of an increasing level of corrosion, and this is supported by a steady increase in the levels of iron present.

Level	Lead	Iron	Copper	Total
slight corrosion	17.69	0.43	72.07	95.68
corrosion	11.98	0.32	76.65	92.44
very corroded	16.82	0.18	72.52	92.84
heavily corroded	9.80	0.41	79.29	94.62
mineralised	7.96	0.84	66.32	91.67

TABLE 10. MEAN VALUES FOR MARKET DEEPING CORROSION GROUPS

The totals are also somewhat lower than is usually acceptable for compositional analyses. However, duplicate analyses have confirmed their accuracy, suggesting the presence of an element, or elements, not analysed for by AAS. The analysis of the surface of one of the coins by EDAX (see chapter 2) suggests the presence of chlorine and phosphorus in small, but significant amounts (see appendix 3). Lighter elements such as oxygen, hydrogen and carbon, undetectable by the analyser, are also lkely to be present.

However, these figures only *suggest* trends attributable to the effects of corrosion. The differences in the types of coin represented must also have a part to play. Nevertheless, on the basis of the forgoing studies, it is felt that the trends shown in the variables presented here are more likely to be a function of the corrosion level than a function of the archaeology and are not investigated further.

As a further experiment it was decided to run principal component analyses on the group as a whole to see if the extreme corrosion suffered by these coins in any way interferes with the compositional groupings of issue and/or status as a copy or as an 'official' issue.

The first analysis was conducted on all the elements analysed (excluding copper) and produced the plot in fig. 46. This clearly separates the radiates and their copies from the later coins but also divides into two very different groups along the first axis. A look at the component loadings clearly shows that the first component is largely describing the zinc contents. This is important, given the known presence of zinc in radiate copies (chapter 2). Indeed the group to the far right of the plot, defined primarily by a higher zinc content, consists of three known copies and one presumed 'official' coin. However, the 'official' coin is heavily corroded, the

attribution being tentative. The remainder of the coins are clustered together, copies and 'official' coins together, showing little significant structure.

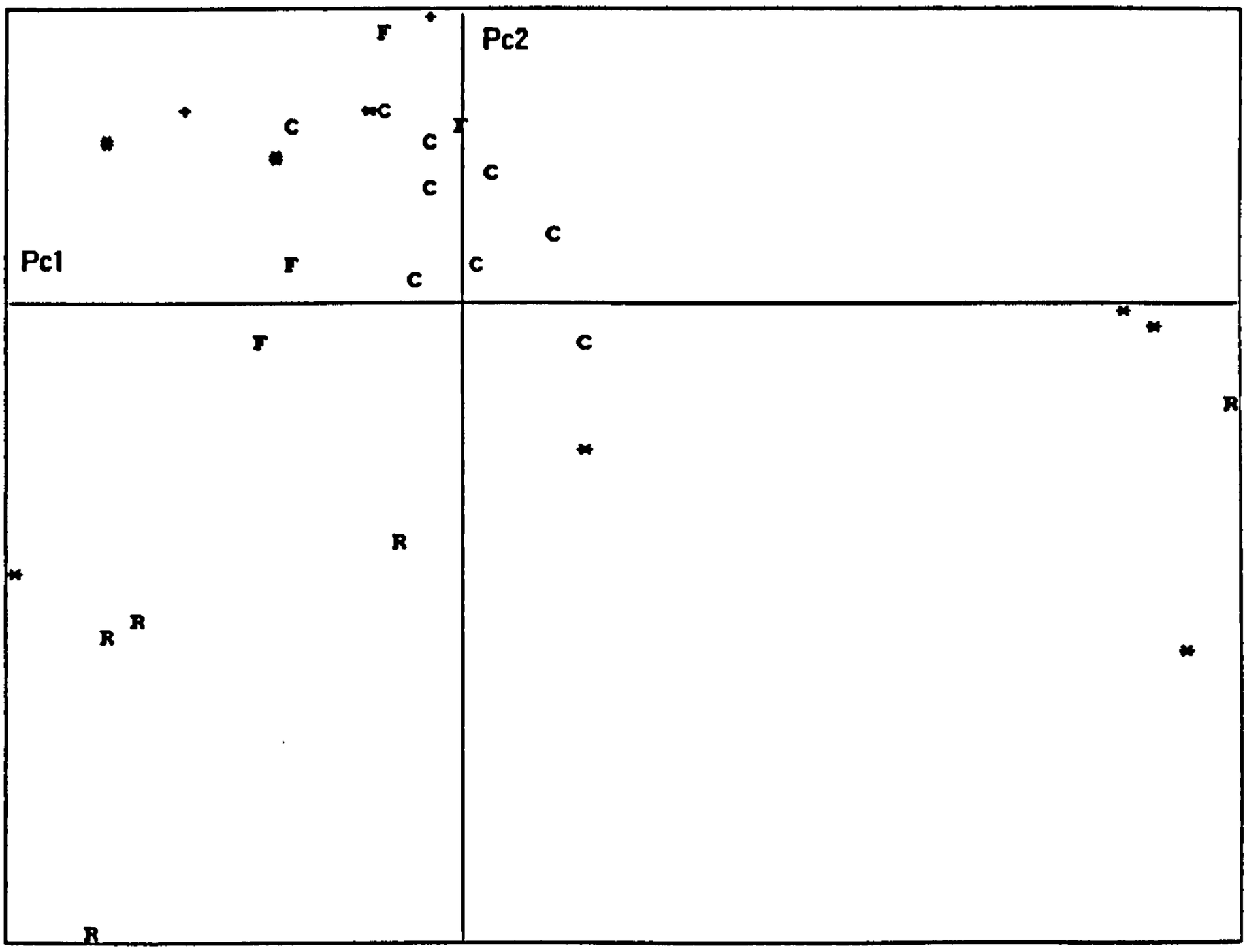


FIG 46. PCA PLOT OF ALL MKT.DEEPING COINS: ALL ELEMENTS

R Radiate ***** Radiate copy **C** Constantinian **+** Constantinian copy

F Fel. Temp. **#** Fel. Temp copy

A second principal component analysis was conducted on the same data set but with the radiates and their copies taken out. The resultant plot (fig.47) shows a tentative separation of the 'copies' from the 'official' issues of both the Constantinian copies and the 'Fel. Temp.' copies. This is, unsurprisingly, due to a combination of silver, iron and tin, iron being the most significant. Repeat PCA's using a divided data set showed some separation on the basis of the major components (silver, tin and lead), although less clear. The principal component analysis using the minor and trace components produced no significant groupings.

In order to directly compare all the groups in the Market Deeping material with numismatically similar coins from benign hoard environments a replica data set was made up. This was composed of the analyses of coins from the hoards discussed above, randomly selected and assembled in the same proportions as the data set from the Market Deeping assemblage.

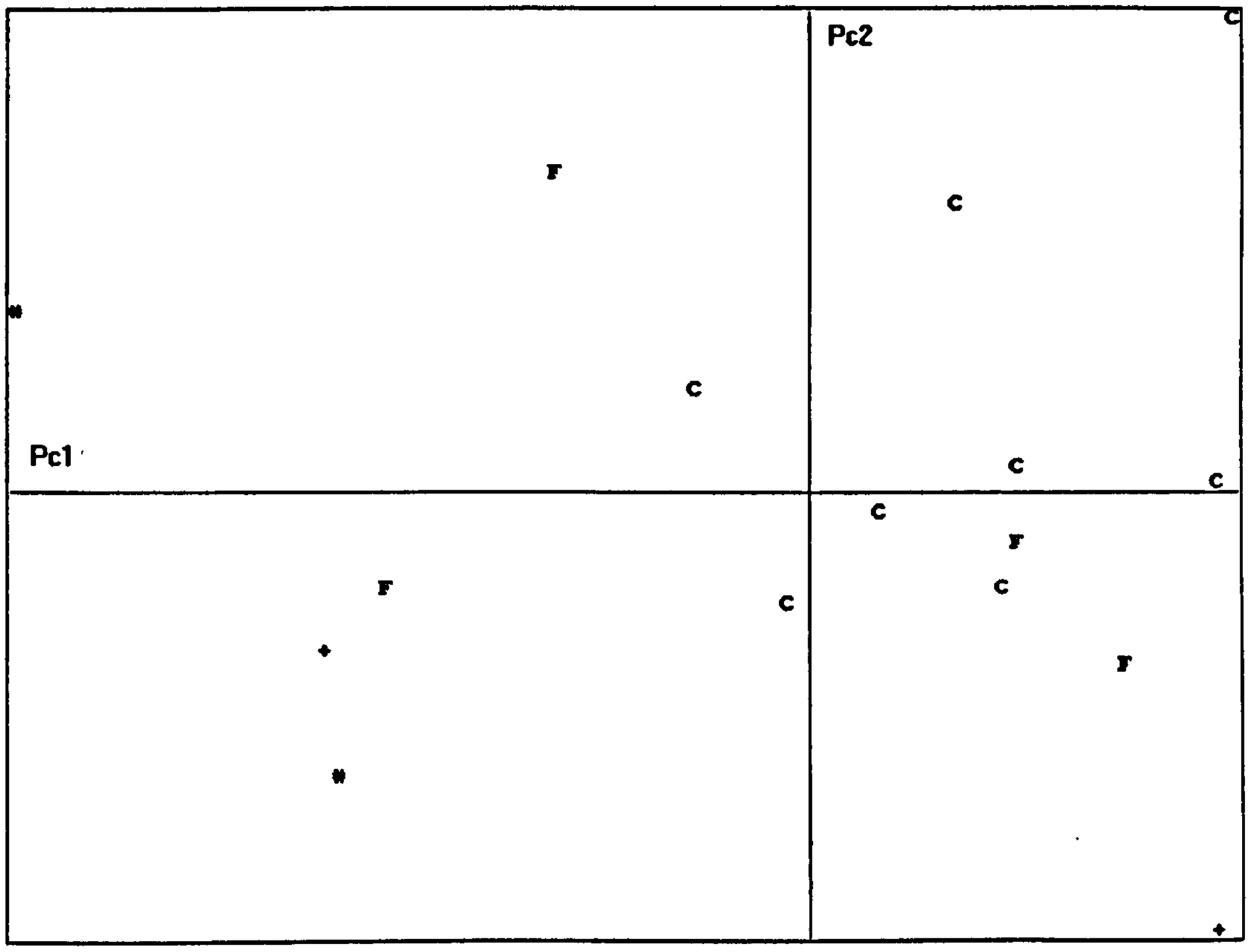


FIG. 47. PCA PLOT OF DEEPING CONSTANTINIAN AND FTR ISSUES: ALL ELEMENTS

The same PCA were conducted on this data set as were conducted on the Market Deeping material. The resultant plots are shown in figures 48 and 49. The plot using all the data compares reasonably well with that of the Deeping coins.

The radiates (both 'copies' and 'official' issues') are well separated from the rest, and are themselves divided between 'copies' and 'official' issues along the first axis. This axis is essentially describing the zinc contents as in the Market Deeping analysis. A comparative table of variable loadings is given below (table 11).

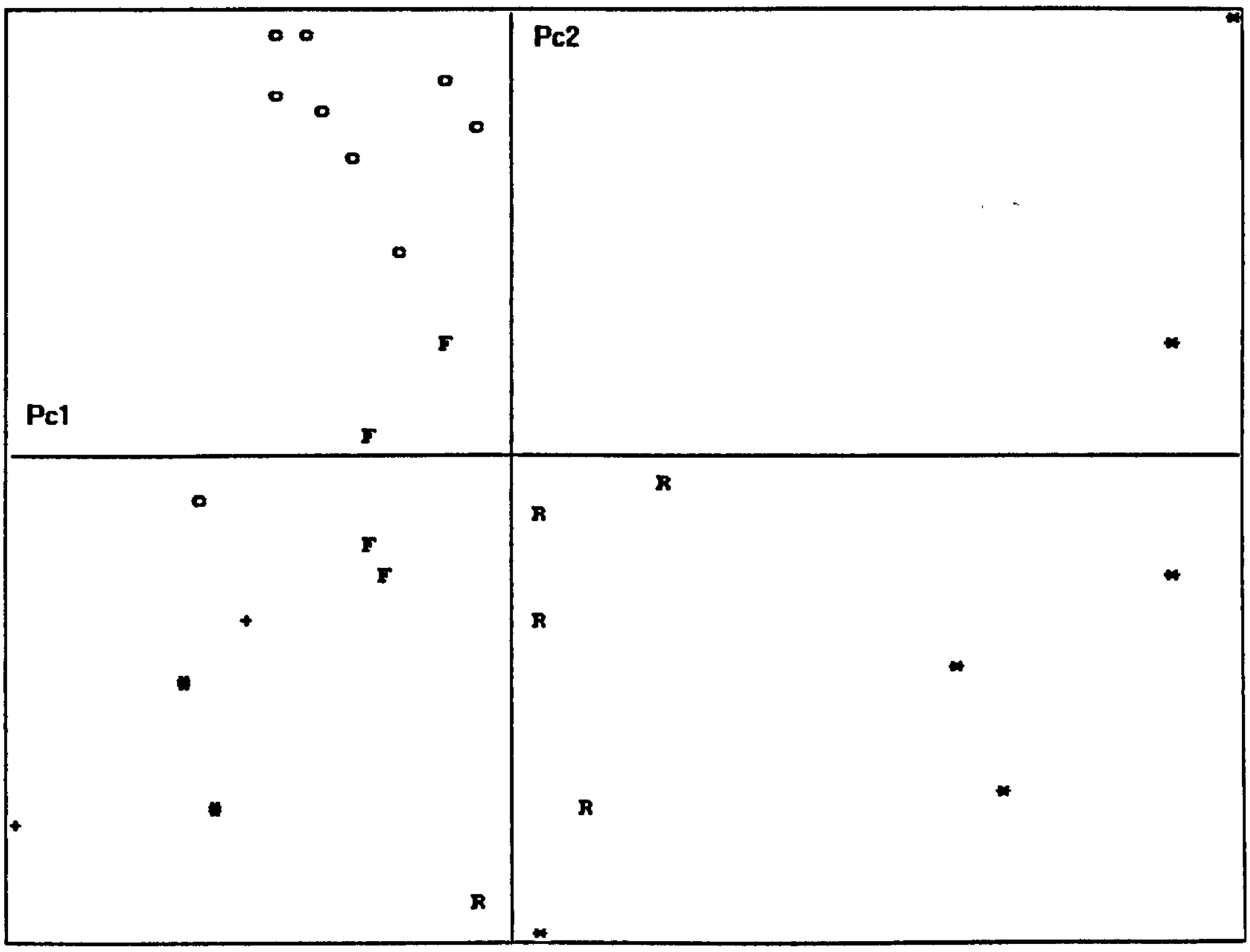


FIG.48. PCA PLOT OF DEEPING REPLICA GROUP: ALL ELEMENTS

Element/Variable	Market Deeping		Replica Data Set	
	Pc1	Pc2	Pc1	Pc2
Tin	0.86	0.24	0.46	0.13
Lead	0.26	1.10	-0.47	0.26
Silver	-0.61	-0.31	0.02	0.27
Zinc	1.45	-0.46	1.49	0.14
Nickel	-0.10	-0.25	-0.18	0.14
Iron	0.13	0.35	0.24	1.30
Arsenic	-0.10	0.11	-0.19	0.02
Cobalt	-0.17	-0.07	-0.16	-0.04
Chromium	-0.02	-0.04	-0.80	0.50

TABLE 11. VARIABLE LOADINGS

The second axis (component) of the replica (hoard) data analysis is essentially describing the iron levels. However, the Market Deeping analysis clearly shows lead to be the major contributor to this axis. This may well reflect the greater variation in the lead levels caused by the severe

corrosion. This appears to have masked out the variability of the iron which is responsible for the archaeologically significant variation.

The plot of the principal component analysis conducted on the hoard data with the radiates removed is also broadly similar to the Market Deeping plot of the same subset. The copies of both the Constantinian and FTR issues are clearly separated to the bottom left of the plot. The main differences are in the degree of separation. The hoard material shows a much more discrete separation between the archaeological groups, especially between the 'official' Constantinian issues and the 'official' FTR issues. The fact that in each analysis one coin identified as 'official' is grouped with the copies merely demonstrates the fallibility of conventional numismatic identification. What is of interest is the way that the general grouping are mirrored in both plots, but that the Market Deeping groupings show considerably more overlap between the Constantinian issues and the FTR issues. The variable loadings in both cases show that the first component is essentially describing the iron contents. This is not surprising as iron has again been identified as an important distinguishing element in both the studies of the Bancroft and Stoneykirk hoards above. The loadings on the second component are different. The hoard material axis is largely describing an opposition between silver and cobalt on the one hand and chromium and lead on the other. The Market Deeping material shows no single element making a significant contribution, although there is an opposition between nickel and iron.

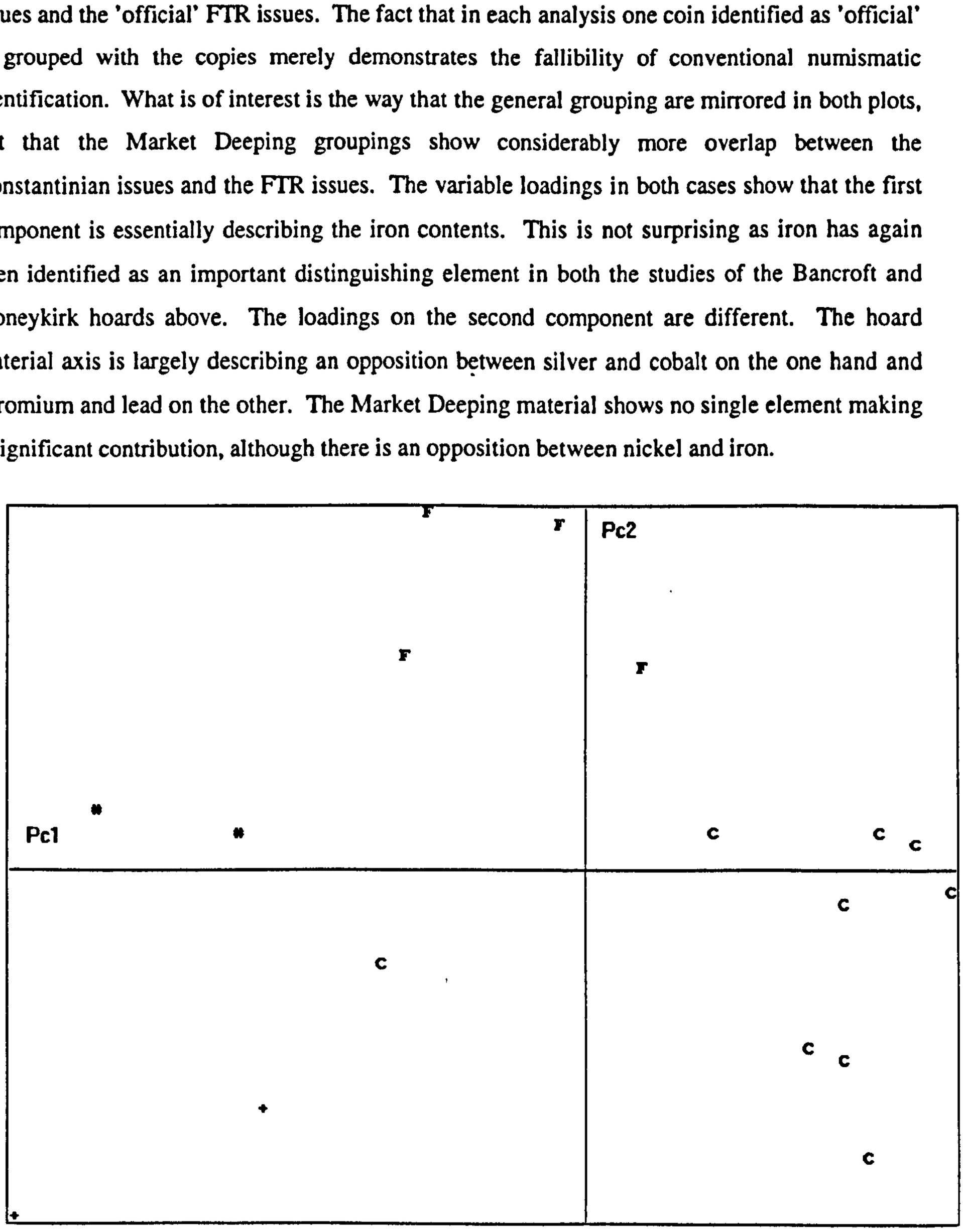


FIG. 49. PCA PLOT OF REPLICA DATA SET WITHOUT RADIATES: ALL ELEMENTS

3.4.3 Discussion and conclusions.

The statistical analysis of the data from this analysis demonstrate that analyses of corroded material may yield data that could result in archaeologically misleading conclusions. The groupings are retained in the principal component analysis, but are often less clear than those produced by un-corroded material. The masking effects caused by the variability engendered by preferential corrosion may result in archaeologically significant variability being obscured. The general trends appear to remain - thus the zinc in the barbarous radiates remains to distinguish between copy and prototype. However, the small, but often important, variations in minor and trace components can become confused by the effects of the corrosion processes.

The coarser differences between classes of coin or issue remain sufficiently clear in corroded material to enable compositional differentiation. However, the more subtle differences between certain types of copy, mints or particular batches of metal will be obscured and altered by the effects of corrosion. The intrinsic variability in certain elements, such as lead, appears to become magnified by corrosion, whereas others remain un-changed.

Chapter Four:
A Discussion and Critique of the 'usual' Methodologies.

"The path is clear
Though no eyes can see
The course laid down long before.
And so with gods and men
The sheep remain inside their pen,
Though many times they've seen the way to leave."
(P.Gabriel 1973)

4.1 Introduction

So far this thesis has looked at the development of compositional analyses of copper-alloy coinage alloys and how these analyses have been used to increase our knowledge of ancient technologies and economies. It has also discussed the theoretical difficulties inherent in carrying out a program of analyses which will produce results which are sufficient to prove archaeologically/numismatically useful. The last chapter described a series of case studies where careful analyses of specially selected material was used to investigate certain archaeological/numismatic questions. It was also suggested that the validity of such analyses can be called into question when analyses of coins from different sources are compared and especially where differing degrees of corrosion are represented.

This next chapter takes this final theme further, investigating how serious the differences between surface and bulk analytical techniques can be, how marked variation can be between differing levels of corrosion of numismatically identical material, and the importance of a rigorous analytical procedure.

4.2 Comparison of numismatically identical material by AAS and XRF.

4.2.1 Introduction

A number of published articles have dealt with the problems perceived as inherent in the bulk analyses of copper-alloys. Carter (1964 and 1967) discusses the application of x-ray fluorescence in the analysis of ancient coins. In particular the work of Carter et al (1978), Carter and Kimiatek (1986), and Carter et.al. (1983) demonstrated the reliability of x-ray fluorescence analyses for bulk analyses of relatively pure, homogeneous copper and brass (orichalcum) coins given careful and adequate surface preparation. However, the findings of Carter's work need to be seen as specific to the alloys investigated, which are, of course, relatively homogeneous single-phase materials (fig.50). Indeed, Carter himself states that,

> "Concentration gradients in coins at and near the surface appear to occur only in certain highly alloyed coins; in these coins differences will obviously occur between XRF determinations and analyses made by other methods" (1983.203).

Nevertheless, the procedures discussed by Carter (1967, 1980, etc.) have, on several occasions, been applied to coins for which they are not suitable (Ziegler 1983 and Carter 1983 for example). One example of this, involving material appropriate to this study will be assessed.

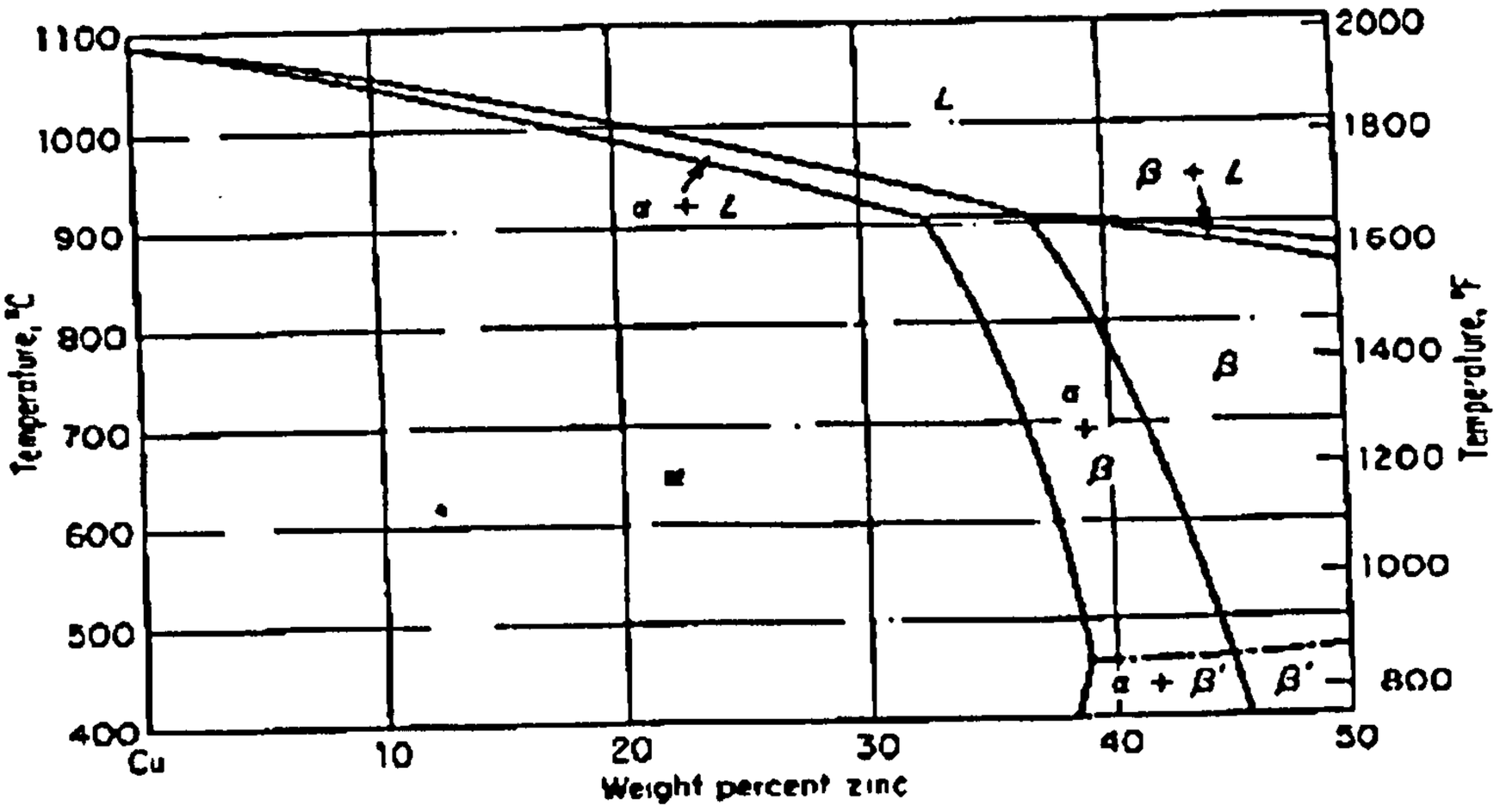


FIG. 50. COPPER-ZINC PHASE DIAGRAM

The work of Ziegler (1983) on material from the Brauweiler hoard used XRF to analyse a large number of mid-third century radiate coins. The preparation technique employed is somewhat similar to that suggested by Carter (1964) , involving the removal of the 'patina' (1983.88), although unfortunately the exact method is not reported. The method of analysis is interesting, involving the rotation of the coin at 60 rpm "...in order to level out heterogeneities" (1983.87). This is done to both the obverse and reverse of each coin and then the arithmetic mean is calculated for each result and the whole set then normalised to 100%. Justifications are given for this method (1983.87), and it is accepted by Ziegler that the rotation method does <u>not</u> compensate for the relief of the coin resulting in low copper readings. This fact alone would then cause innacuracies in the other metals detected upon normalisation to 100%.

Although no single analytical technique and its methodology is able to escape some criticism, it is readily apparent that the method adopted by Ziegler (1983) allows a margin of error that is unacceptable for anything other than semi-quantitative approximations. The cleaning method adopted is not reported, which is in itself an important omission. We can, however, assume that it was not too dissimilar from that of Carter (1964), involving the removal of the surface layers. The method used by Carter involves first electrolytically cleaning the coin cathodically (negative electrode) in a solution of hot sodium carbonate, this is to loosen any dirt remaining which is then removed with a pencil eraser. The coin is then dried and abraded with aluminium oxide powder, removing an estimated 10 - 15 μm of metal (Carter 1983.23). This technique has proved itself

with simple binary alloys and fundamentally pure copper coins as discussed above, but it is felt that its application to the more commonly encountered complex alloys is inappropriate and liable to produce erroneous results. Furthermore, the electrolytical cleaning can also result in the reduction of some corrosion products to metal. These can either fall off into the solution or be *re-deposited on the coins surface* resulting in a further likelihood of erroneous data.

In order to test this hypothesis a number of the coins from the Walbottle hoard analysed for this project were chosen to be numismatically identical to issues analysed by Ziegler (1983). Comparison of Zieglers results with those conducted by the author using AAS on coins of the same issue from the Walbottle hoard produced significant differences. Although there is inevitably going to be some variation in composition within any given issue (see section 4.3.2), it will be demonstrated that the differences encountered in this study are a product of the differences in analytical technique rather than burial environment or natural variation. Both groups of material are from well preserved hoard material.

The most pronounced difference is in the lead contents. It is the magnitude of this difference which is of particular note. The table below (table 12) lists the mean lead contents of particular issues analysed by both AAS and XRF together with some wet chemical analyses;

Issue		AAS (%)	XRF (%)	Gravimetric (%)
Claudius II.	RIC 91	12.8 (1)	0.8 (1)	
	RIC 104	7.5 (1)	0.7 (1)	
	RIC 109	10.3 (2)	0.3 (4)	
	RIC 261	10.9 (2)	3.1 (24)	9.8
	RIC 266	9.8 (2)	0.8 (10)	6.2
Victorinius.	E 741	2.6 (2)	0.2	
	E 699	1.9 (2)	0.2	
	E 732	1.1 (2)	0.3	
	E 682	1.6 (4)	0.1	0.2
	E 633	1.6 (4)	0.2	
Tetricus I.	E 774	1.2 (2)	0.3	
	E 764	2.1 (2)	0.3	
	E 786	2.0 (1)	0.2	
	E 775	1.3 (2)	0.2	1.84
Tetricus II.	E 769	1.3 (2)	0.2	
	E 778	2.5 (1)	0.2	

TABLE.12. COMPARISON OF LEAD CONTENTS BY XRF, AAS AND GRAVIMETRIC TECHNIQUES.

The differences in the results obtained by the two main methods above are significant, and it is notable that three of the four gravimetric analyses obtainable are considerably more in agreement with the AAS than the XRF. Furthermore, a t-test (Norussi, 1988) taking all AAS and XRF results for the coins of Claudius II only (RIC91,104,109,261 and 266) gives a t-value of 7.90 with seven degrees of freedom which allows us to reject the hypothesis that the data sets are similar with >99% confidence.

A number of other elements exhibit differences in concentration when analyses are compared, notably zinc, tin and silver. However, when the two data sets are plotted, the differences are not as obvious as they are for the lead values. Consequently, it was decided to use t-tests (Norussi 1988) to test the similarity between these data, as was done with the lead;

	t-value	**degrees of freedom**
Lead	7.90	7 df
Tin	7.42	46 df
Silver	1.93	45 df
Zinc	3.07	42 df

TABLE 13. COMPARISON OF MAJOR COMPONENT VALUES FOR ISSUES OF CLAUDIUS II.

As can be seen in the above table, in all cases the t-value was >1.90, and for two out of the three elements >3.00. As the plot would suggest, silver is, perhaps oddly, showing the greatest ambiguity. Nevertheless, the result of the T-test would indicate that the differences in analytical technique are significant, for silver, tin and zinc concentrations as well as lead.

Comparison of the AAS data with Zieglers' (1983) XRF analyses for the issues of the Gallic Empire (Elmer reference numbers) was complicated by the fact that only the mean values were published without their standard deviations. However, it was felt appropriate to conduct t-tests substituting the standard deviation of the AAS data as an estimate. This method produced the following t-values;

	t-test	**degrees of freedom**
Lead	10.10	33 df
Tin	4.26	33 df
Silver	0.00	33 df
Zinc	>3.88	33 df

TABLE 14. COMPARISON OF MAJOR COMPONENTS FOR GALLIC ISSUES.

From these results it is apparent that the lead, tin and zinc values are significantly different to a 99% confidence level, thus confirming the incompatibility between the analytical procedures employed. The silver values, however, are less straightforward. The apparent statistical similarity can be explained if one considers that this element has the highest variance (0.28) and also the greatest standard deviation (0.53). Furthermore, the existence of two marked outliers of 2.28% and 2.16% would also account for the apparent similarity of the means. If these two outliers are removed and the t-value recalculated then a figure of 0.435 at 31 degrees of freedom is obtained. This still remains too small for a greater than 90% confidence level, but is, nevertheless, an improvement on the raw data calculation and, furthermore, still exhibits the third highest variance (0.14) and standard deviation (0.38). It is the lead that, unsurprisingly, exhibits the greatest variation, and it is likely that silvers' affinity for lead is responsible for this phenomenon.

It is therefore apparent from this discussion that there is significant variation between the results of analyses using XRF and AAS conducted on material that should exhibit reasonable similarity, especially over multiple analyses. It is, therefore, important that these differences be examined.

A number of factors may contribute to this phenomena, or a combination of factors. The basic, incontrovertible facts are;

1) The lead contents of these argentiferous copper-alloys established by AAS are considerably higher than those detected by XRF.

2) The zinc contents are likewise generally lower by XRF than by AAS. The few incidences of zinc being higher by XRF than by AAS tend to be so marked as to cast doubt on the current attribution of the coin as a regular issue. As discussed above (chapter 3, section 1.2) irregular coins of this period are usually marked by a significant zinc content, whereas official coins, unless orichalcum, have the merest trace.

3) The tin contents fall into two groups; those with ≅5% tin yield consistently higher results by AAS, whereas those coins with <1% tin are consistently yielding higher results by XRF.

4) The silver contents, as discussed, are more problematic. It does appear, however, that the earlier issues of Claudius II are seen to yield higher silver contents by XRF than by AAS. The later commemorative issues (RIC 261 and 266) have XRF silver values ranging from 2.4% to 0.1% (Ziegler 1983.26). This is perhaps consistent with the numismatic history of the issues, which also degenerate significantly in style. Indeed, Ziegler mentions the activities, referred to in the literature, of the influential "rationalis" Felicissimus, who was executed for issuing, or permitting the 'private' issue of 'bad' coin (1983.93). It appears that coin metal had been embezzled during the first months of Aurelians reign (when the Claudius II commemoratives were issued) and that, when discovered, Felicissimus tried to incite a mint workers revolt;

"And also inside the city (of Rome) the officers in charge of the issue of coinage were killed, who had, under the direction of Felicissimus debased (corrupted) the official coins." (Aurelius Victor 35.6)[6]

This historical factor is likely to contribute to the problematical nature of the silver contents, especially as a concentration gradient with time exists within a specific issue. Nevertheless, this is only a part of the story. The metallurgy also has a major part to play and the reasons for these observed phenomena will be discussed below.

In order to investigate why we have this apparent difference in results between two analytical techniques it was decided to look at the distribution of the various constituent elements within the coin in order to establish the degree and depth of any enrichment/depletion phenomena.

Permission was gained to remove metallographic sections from four of the Walbottle hoard coins. These were then mounted in polyester-resin following the usual metallographic preparation technique and polished with diamond pastes down to ¼ micron. The coins chosen were two radiates of Claudius II (RIC 91 and RIC 104), a radiate of Victorinius (Elmer 683), and a radiate of Tetricus (Elmer 764). Each of the coins had been previously analysed by AAS.

Once mounted and polished, the sections were analysed by a Jeol JSX-8600 Electron Microprobe (EPMA) using, initially, a routine which produces a concentration dot-map of a specified area of the sample for given elements. Seven elements were chosen for mapping: silver, tin, lead, zinc, arsenic, iron, nickel, and in some cases, copper. The sensitivity of an EPMA is such that trace levels of most elements are detectable, provided an accurate calibration is achieved using pure-metal standards. The standards used for all the EPMA work in this thesis were chemically pure metal standards, except in the case of lead, where a galena (PbS) standard was used.

Once the concentration maps were studied, the composition of the different phases was assessed. To do this a beam, usually between 2 and 5 μm, was focused on the area in question and a quantitative analysis run. A condition file was set up using the same standards as before, and the ZAF correction routine was used in all cases where quantitative analyses are quoted. Normalised values are given, except where otherwise stated.

Operating parameters were maintained consistently throughout the analysis of all samples. An accelerating voltage of 20 Kev was used, with the current maintained in the region of 1.4E-8

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6 "Neque secus intra Urbem monetae opifices deleti, qui, cum auctore Felicissimo rationali nummariam notam corrossient, poenae metu bellum fecerant usque eo graue uti, per Coelium montem congressi, septem fere bellatorum millia confecerint." (Aurelius Victor 35.6)

A. Having two spectrometers it was possible to chose lines with the minimum of spectral interference, even if different crystals were required. The following lines were generally used;

Element and line	Wavelength and crystal
As Kα	73.44 LIF
Ag Lα	133.06 PET
Pb Mα	169.31 PET
Sn Lα	115.28 PET
Ni Kα	115.12 LIF
Cu Kα	107.12 LIF
Fe Kα	134.82 PET

The Mα line was chosen for lead because, although weaker, it does not overlap with the arsenic line and it was felt that the quantities of lead present would be sufficient for a precise analysis.

Because of the initial difficulties of obtaining high quality colour hard-copy of the concentration maps it was necessary to photograph the monitor screen. This is not ideal; slight distortion occurring due to the curve of the screen, and occasional problems due to reflection of the glass of the screen. However, the colour differentiation is far better than from a die-link transfer printer, and the whole screen is captured including the scale.

Each concentration map has a scale (usually in microns) at the top right of the image, and a colour scale at the bottom right. The colours correspond to the degree of concentration; the higher concentration is at the top of the scale, the lowest at the bottom. Colours were usually selected automatically, although some of the more unpalatable colour schemes were manually altered.

4.2.1.1 Study No.1; RIC 91, radiate of Claudius II (Sample No.28).

The area chosen for concentration mapping is about 1.7mm by the thickness of the coin (1.5mm), and includes the very edge. The AAS analysis gave the following results; 1.28% silver, 5.75% tin, 0.047% nickel, 0.047% iron, 12.82% lead and 0.02% arsenic. The XRF analyses conducted by Ziegler (1983) on a numismatically identical[7] coin gave 1.5% silver, 5.0% tin and 0.8% lead (see t-tests in section 4.2.1). The silver and tin values are fairly close, the differences explainable by normal surface enrichment and depletion. Plate 11 shows the silver concentration map. There is a clear increase in silver concentration to the middle of the outside edge, and, although patchy, it is possible to discern a slight increase in concentration at the top and bottom

[7] By 'numismatically identical' what is meant is a coin of exactly the same issue and mint.

(corresponding to the obverse and reverse faces of the coin). This phenomenon is made clearer in Plate 12, which shows a reduced (and less clear) concentration map, together with a line scan across the area between the two vertical lines superimposed on the concentration map. The heterogeneity of the silver is very apparent, as is the enriched zone immediately below the surface.

In understanding these analyses it should be remembered that no surface treatment/cleaning had been attempted. Consequently the very edges of the concentration maps will include the surface corrosion layer. This is usually very thin on material this well preserved (usually a couple of microns) but will be picked out by the change in concentration of most elements featured. Here the decrease in silver in this layer is readily apparent.

Despite the increased amount of tin present (5.75% tin compared to 1.28% silver by bulk AAS), this concentration map (Plate 13) appears sparser, this is because of the reduced sensitivity of the tin line and could have been overcome by an increased count time had it been deemed necessary. Nevertheless, what is of interest here is the way that the tin is concentrated on one side of the coin as well as in the centre of the edge. The line scan again shows this more clearly (Plate 14). The reasons for this distribution become clear when we look at the lead concentration map (Plate 15). Here we see the same pattern, only more pronounced because of the larger amount of lead present and the greater sensitivity of the line. Also the almost total insolubility of lead within the copper matrix means virtual mutual exclusivity. The similarity of the distribution of both tin and lead is probably due to gravity segregation during a prolonged cooling period coupled with the mutual solubility of lead and tin. The large number of areas low in lead can clearly be seen, both internally and especially at the top edge. It is this phenomena which is largely responsible for the gross discrepancy between the XRF and AAS analyses. In a more corroded sample more of the discrete lead (and tin) globules would have been corroded out at the surface.

The arsenic concentration map (Plate 16) shows a similar phenomena, although its' greater solubility is readily apparent. There is again an apparent affinity of the arsenic for the lead and tin, which is not surprising. However, the possibility of a spectral overlap between the arsenic line and an adjacent lead line must not be forgotten. The choice of a well separated lead line for analysing lead does not mean that another lead line adjacent to the chosen arsenic line will not interfere with the arsenic determination.

The copper concentration map (Plate 17) confirms the trends shown by the other elements. There are two very obvious areas where the copper concentration has been reduced by the corrosion processes. The topmost edge corresponds to one of the areas of silver enrichment as

well as depletion of tin, lead and arsenic. The same pattern is even more pronounced at the centre of the coins edge. Once outside these areas the copper concentration remains fairly constant with fluctuations caused by much smaller globules of the lead-rich rich phase.

The unetched photomicrograph of the same area (Plate 18) also shows the large number of voids left by trapped gasses during cooling of the blank after casting. The incursions of corrosion can also clearly be seen, especially at the centre of the coins edge. Much of this is caused by the preferential corroding out of the lead-rich phase which was squeezed to the edges of the blank during cooling and by striking and to the bottom edge by gravity.

Plate 19 shows a close-up of the corroded-out centre edge. Within the corrosion products discrete grains of silver-rich lead alloy can be seen (see table 15 below), corresponding very closely to the distribution shown in the concentration map. The same can be seen in the secondary electron image (SEI) (Plate 20), the corroded area appearing darker than the copper matrix, the lead-rich phase appearing lighter.

The corroded and subsequently enriched area at the centre of the coins edge is an interesting feature. By the shape of the coin's edge it is possible to suggest that the action of striking the coin produced this 'folded' effect. The energy expended in creating the fold and subsequent deformation of the structure would result in making the area much more susceptible to corrosion (Avner 1988.594). This is an important observation given the common practice of conducting XRF analyses on the polished edges of coins (c.f. Walker 1976).

From the above study it is apparent that the composition of this coin differs dependent on the area of the coin on which the analysis is conducted. Even if a surface preparation technique akin to that of Carter was utilised, the removal of 15 µm is by no means sufficient to overcome all the concentration gradients shown here. Taking the copper concentration map (Plate 17), it is readily apparent that a minimum of between 50 and 100 µm would need to be removed before an area of un-depleted copper-alloy is found. This, by itself, is a crucial consideration where normalised figures are used, as is usual for XRF and associated techniques.

EPMA is a technique which requires the sample to be highly polished and mounted so as to be at exactly 90° to the electron beam. If this is not the case, then inaccuracies in the detected energies can occur (Potts 1987.346). Because of this factor it was important that the phenomenon apparent on the concentration maps was 'real', and not a result of the samples topography. In order to test this a series of point analyses were conducted on an imaginary line running from the middle of the coin to its very edge. Each point was approximately 10 µm from the previous point, and each analysis was run three times. This was done for each element mapped and in

approximately the same area. The mean values were then taken for each point and then plotted against depth as a line graph. The graph for silver is shown in Figure.51.

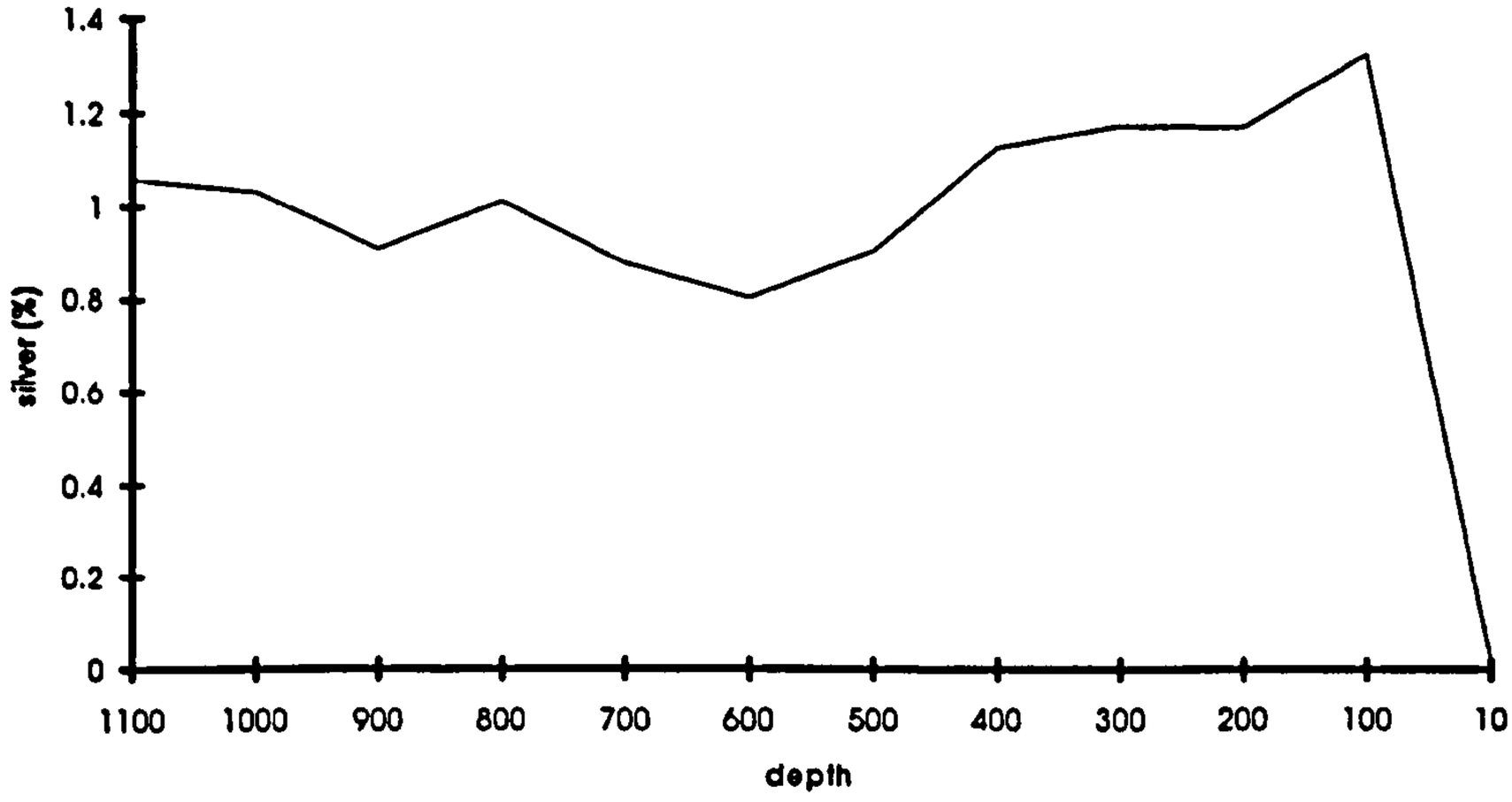

FIG.51. PLOT OF SILVER CONCENTRATION ACROSS DEPTH(μm)

This plot shows the increase in concentration towards the surface of the coin commencing from about 400 μm and dropping off markedly at about 10 μm (in the corrosion layer). This confirms the accuracy of the trends shown in the concentration maps and the plots for the other elements do the same.

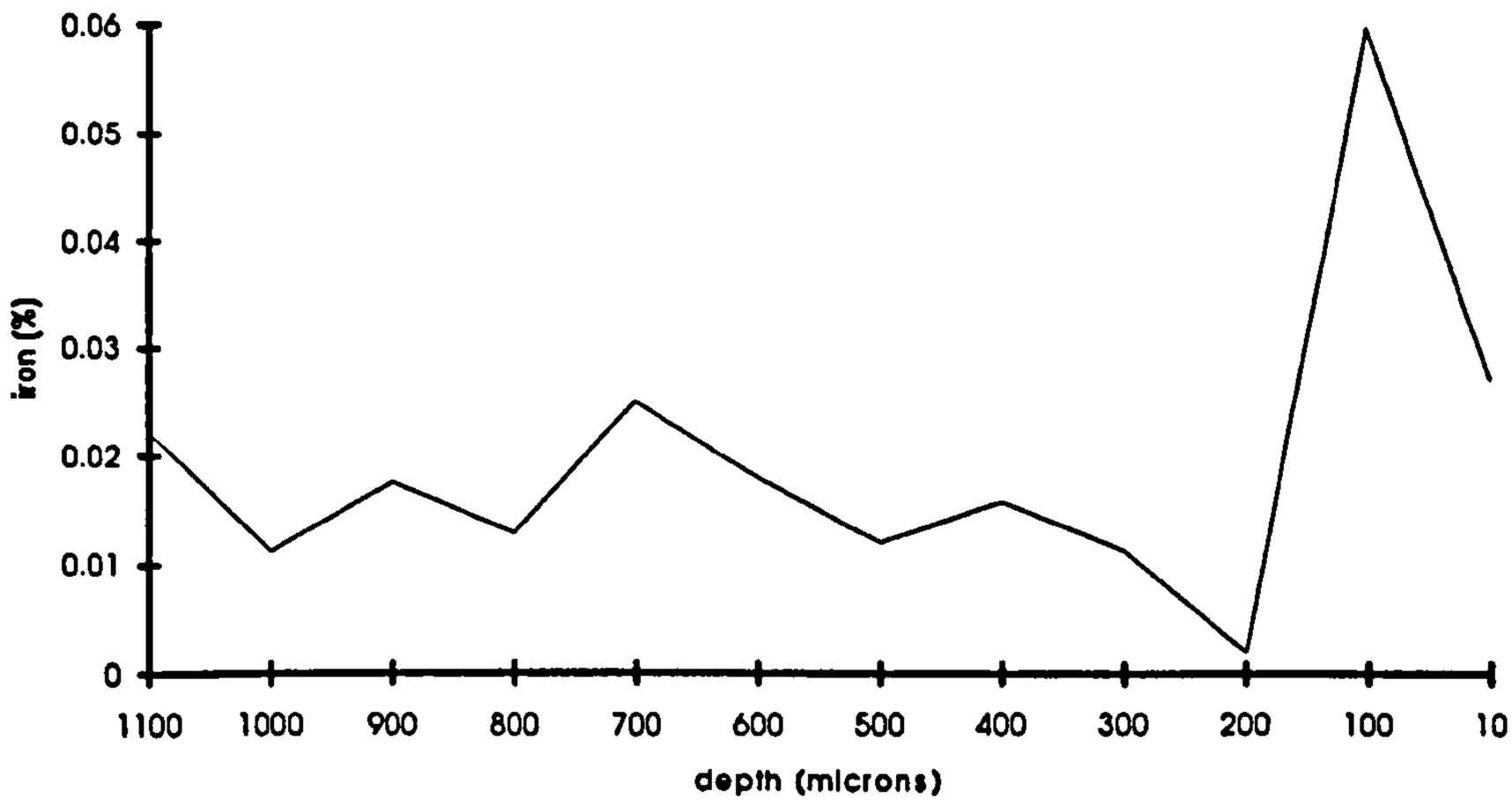

FIG.52. PLOT OF IRON CONCENTRATION ACROSS DEPTH.

The plot for iron (Fig.52) in fact shows a greater increase in concentration towards the coins surface than is apparent in the concentration map (Plate 21). This is because the colour bands used in this map are computer selected and broader than the differences picked up in the plot.

The variation in the iron content is only a matter of ≅0.05%, but enough to be significant in any statistical analysis.

Although not corroded to any obvious degree, the increase in iron at the coins surface is likely to be a consequence of the iron from the ground water percolating into the voids in the copper matrix left by the preferential corrosion of the lead-rich phase. This is what one would expect going by the results discussed in the previous chapter.

The nature of EPMA means that it is possible to analyse with considerable accuracy very small areas. This can be seen as a disadvantage of the technique (see Cope and Warren 1974. 237-247) especially where reliable bulk analyses are required. However, in this instance, reliable bulk analyses had been obtained by AAS. Consequently, it was decided to utilise the much improved micro-analytical capabilities of modern EPMA to study the different phases visible, and to compare these with the bulk analyses in light of the optical microscopy. Plate 22 shows an etched photomicrograph of the approximate area chosen for this analysis. It is adjacent to the surface in order to pick-up sufficiently large inclusions for an accurate EPMA. The structures shown are fairly typical; fairly large, equi-axed grains, some twinned which have been distorted by the action of striking. Between some of these are gas voids and the different phases, visible as inclusions, analyses of which are discussed below. The absence of strain lines, distribution of phases and presence of twins would suggest that the cast blanks were annealed and hammered flat first before being hot-struck.

The analytical results (normalised) are summarised in table.15. The AAS results are included for comparison as the bulk analyses. The large inclusions correspond to the larger white globules in the photomicrograph, which turn out to be a silver-rich lead phase. The EPMA secondary electron image (SEI) (Plate 23) shows a highly magnified small inclusion, the analysis of which appears as Small.incl #0 and is mostly lead. The next small inclusion analysed (#1) gave an analysis very similar to the surrounding matrix. This is a common problem encountered when analysing features of less than two microns diameter. This arises from the fact that, although the area struck by the electron beam may only be one or two microns in diameter, the total 'excited volume' (the area of metal emitting secondary x-rays) is somewhat larger and deeper. Thus although the beam may be focused on a two micron inclusion, the total area analysed may well take into account a large proportion of the surrounding matrix. Furthermore, the size of the 'excited volume' is directly proportional to the accelerated voltage being used. For the majority of the work discussed here quite a high voltage of 20 Kev was necessary, which would mean a proportionally large area of excitement (Potts 1987.337).

Location/analyses	Ag	Ni	Fe	Sn	As	Pb	Cu
AAS	1.28	0.05	0.05	5.75	0.02	12.82	80.97
Large.incl #1	5.34	0.01	0.13	11.64	0.88	18.31	59.59
Large.incl #2	3.66	0.09	0.16	1.04	0.00	39.64	55.41
Small.incl #0	0.00	0.00	0.10	0.12	0.00	81.13	18.66
Small.incl #1	1.26	0.05	0.00	4.24	0.07	0.51	93.86
Matrix #1	1.18	0.05	0.04	4.36	0.87	0.54	93.89
Matrix #2	1.27	0.02	0.00	4.65	0.34	0.63	93.10
incl.in.corrosion	4.70	0.00	0.09	0.29	0.99	80.65	13.28

TABLE 15. EPMA OF SELECTED AREAS OF SAMPLE NO.28.

(WT.%)

The two sets of analyses of the matrix are in fairly good agreement, such variation as there is being explainable by micro-segregation at grain boundaries. The beam size used for this particular analysis was 100 microns and would therefore be large enough to include more than one grain. The agreement between the EPMA and AAS is also very good (table 15), the only significant differences being in the tin, arsenic and (most notably) the lead contents. These differences are explainable when one considers the composition of the inclusions, obviously the shortfall in the tin and lead would be made up by the lead inclusions included in the bulk sample. The arsenic, on the other hand, is detected at a significantly higher level than in the AAS analysis. The concentration map shows that the arsenic is distributed fairly well throughout the matrix, with increased concentrations in areas of increased lead/tin/silver, and so one would expect arsenic to follow the pattern of the tin and lead. The fact that it patently does not is probably due to the greater solubility of arsenic in copper[8] . Furthermore, the greater concentrations of tin, silver and arsenic within the lead-rich phase demonstrates the greater solubility of these elements in lead as opposed to copper.

The analysis of the metallic inclusion within the corrosion products (as shown in Plate 19) is interesting. The main constituent is lead, with significant amounts of silver and copper. This would suggest that the high level of corrosion in this area was because of the presence of large lead-alloy inclusions which corrode preferentially. This would support the suggested cooling and working history of the coin discussed above.

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[8] Arsenic has a solubility of 6.9% at 200°C, lead is virtually totally insoluble, tin has a solubility of only 1.3% at 200°C. Obviously much of the 5.75% tin in this coin will remain out of solution, whereas the small amount of arsenic in the alloy means that most will remain in solution (Cope 1972.14).

4.2.1.2 Study No.2; RIC 104, radiate of Claudius II (Sample No.30).

This coin slice was mounted differently to the other three in order to study the changes in concentration towards the coins edge - the area often polished and analysed by surface techniques. To do this a fairly large slice was mounted face down and then ground down to approximately half its original thickness. This section was then subjected to the same set of analyses as the previous sample.

Plate 24 shows the silver distribution over almost the entire sample. The enrichment zone is very clear as is the depletion zone immediately below the surface. If we narrow down to a smaller area (Plate 25) we can see the depleted zone more clearly as well as the enriched zone immediately beneath it. There is a general enriched zone from about 50 μm to ≅200 μm in depth within which are areas of high silver concentration. Beneath this is the bulk area of generally lower silver concentration but with some silver-rich inclusions.

The tin exhibits a similar phenomena to the silver (Plate 26). The large area view again shows an area of enrichment, this time much more uneven and distinct. Increasing the resolution by reducing the area and increasing the number of concentration bands (Plate 27) shows very distinct areas of enrichment immediately beneath the surface, but also a number of large areas of depletion. The depth of the tin-enriched zone is also quite considerable, to the order of 300-400 μm.

The same area mapped for lead (Plate 28) shows a very clear lead-rich phase distributed throughout the coin. The largest of the lead-rich globules are always to be found immediately beneath the surface layer. This layer of ≅20 μm is clearly devoid of large lead particles. The large lead globules are randomly scattered throughout this secondary layer beneath which is a layer generally lacking in lead; it is only beneath this, at a depth of some 400 μm that we reach a distribution pattern which continues relatively unchanged throughout the coin.

A different arsenic line was chosen for this analysis (Kβ 72.92) which is less liable to spectral overlap by an adjacent lead line. The results are shown in Plate 29. There is a clear depletion zone running along the edge of the coin in the same area as the silver and tin enrichment zones. Some of the depleted areas make quite marked incursions of nearly 1mm into the heart-metal of the coin. If this map is compared to the un-etched photomicrograph of the same area (Plate 30) we can see that where the depletion zones extend into the coin there are cracks linking gas voids all the way to the edge of the coin. The depleted areas numbered 1 and 2 correspond to the same in Plate 29 and 3 corresponds to 3 in Plate 31. The same phenomena is apparent on the nickel map (Plate 32), although less pronounced due to both the low levels of nickel present and the

unlimited solubility of nickel in copper. A 50 to 100 micron depletion zone extends along the edge of the coin, extending deeper into the coin along the fissures.

By the same token, there is also a correlation between the tin enriched areas and the fissures. Lead and silver are not so clearly related, although some of the areas depleted in silver are adjacent to fissures.

To confirm the validity of the mapping, sets of multiple point analyses were conducted for each element in the same way as before. Figure 53 shows, as an example, the plot of silver concentration against depth.

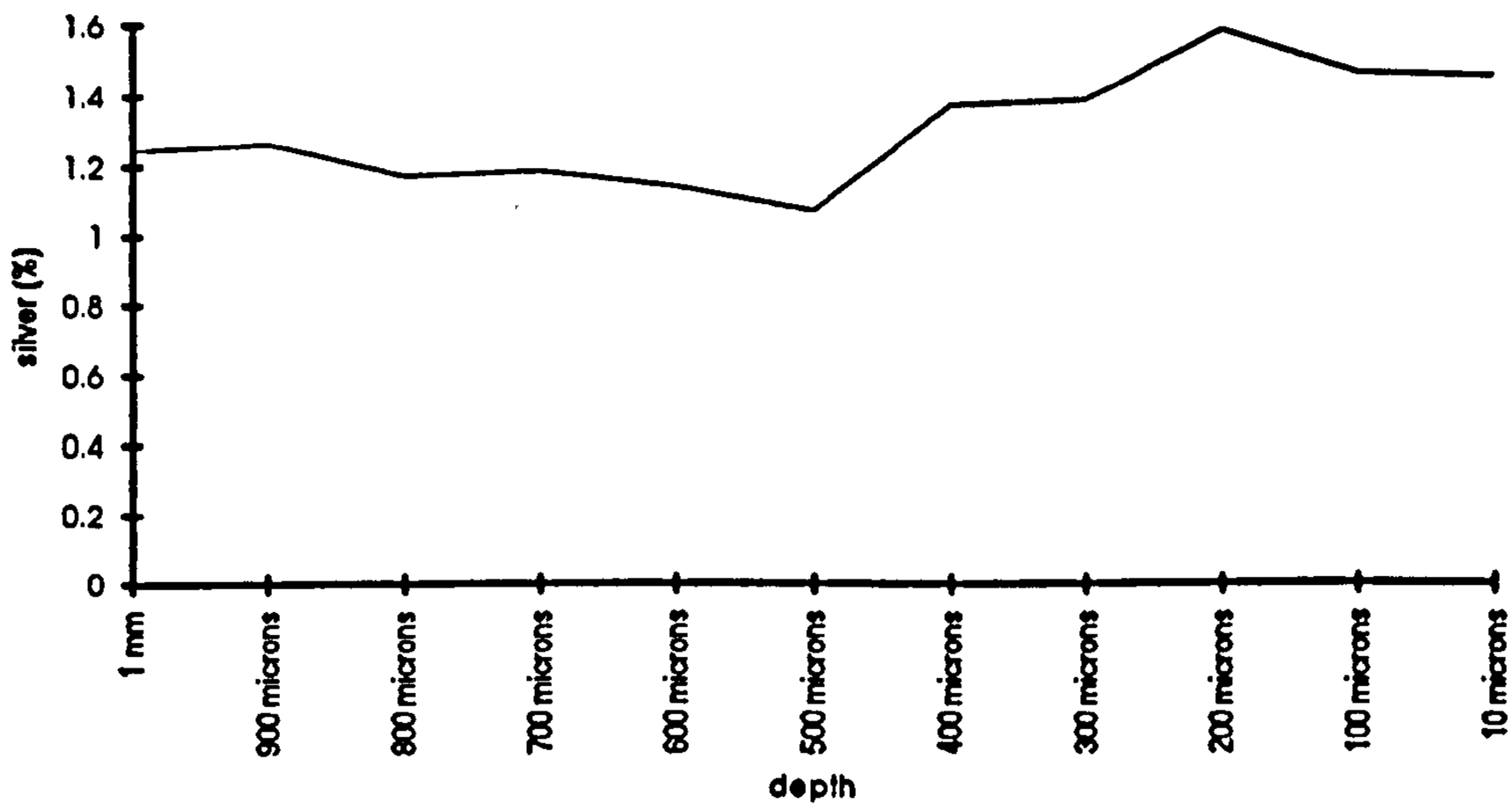

FIG.53. PLOT OF SILVER CONCENTRATION AGAINST DEPTH FOR SAMPLE NO.30.

This plot clearly confirms the enrichment zone from 500 µm to about 200 µm and above this is a relatively depleted zone. Beneath the enriched zone the concentration levels out slightly at about 1.25%, this is slightly lower than the AAS result of 1.34%. However, this is to be expected. The shortfall is made up in the same way as the tin and lead etc, being found in much larger concentrations within the predominantly lead-rich phase inclusions.

The iron content (Fig.54) also repeated the pattern of the previous coin, despite the different orientation. The concentration remains at the 0.1-0.15% level (similar to the AAS bulk value of 0.18%), until around 200 µm beneath the surface there is a marked increase to over 0.2%. This must again be due to the percolation inwards and deposition of iron into voids left by the preferential corrosion of other elements, especially along the fissures previously noted.

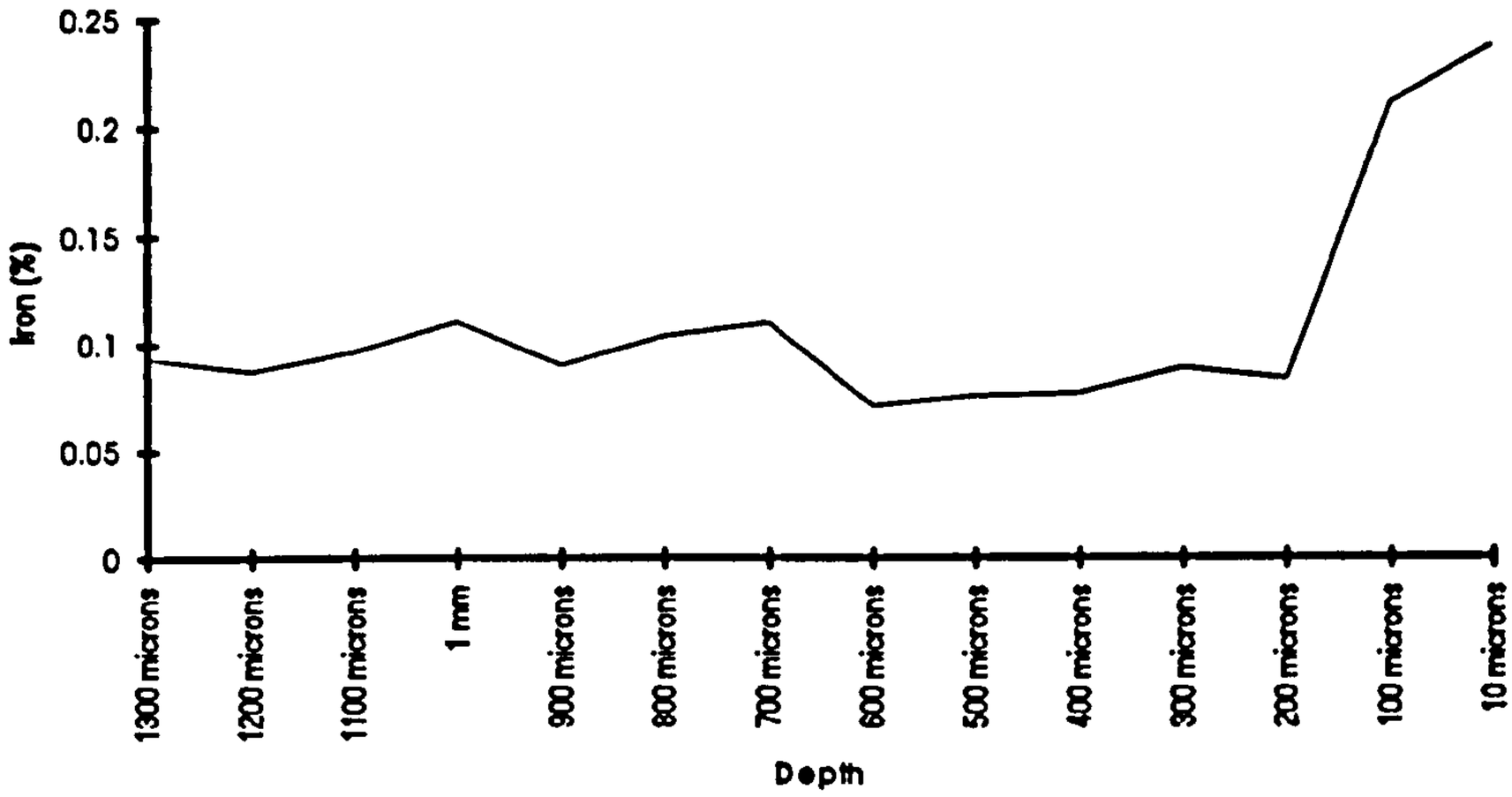

FIG. 54. PLOT OF IRON CONCENTRATION AGAINST DEPTH FOR SAMPLE NO.30.

The etched microstructure (Plate 33) of a part of this sample is, unsurprisingly, very similar to that of the previous coin. Fairly large equi-axed grains have been distorted by striking. Several of the grains are twinned, suggesting that the coin blank was annealed and worked a number of times. The absence of strain lines, the presence of twins and the distribution of the lead-rich phase again suggest that these coins were hot-struck. The layer of corrosion appears as a black, amorphous layer. There are also many gas voids, as with the previous coin, and lead-rich inclusions, some of which are in the process of being corroded out.

4.2.1.3 Study No.3; Elmer 683, radiate of Victorinius (Sample No.62).

The sample taken from this coin was a simple slice in the fashion of the first study. The AAS analysis of this coin gave 1.60% silver, 0.21% tin, 0.03% nickel, 0.07% iron, 1.60% lead and 0.12% arsenic. This shows that this coin is markedly lower in tin and lead than the issues of Claudius II, furthermore, the un-etched photomicrograph (Plate 34) shows considerably less porosity. The distribution of the silver (Plate 35) is consequently rather more even, although there are still, as with the previous coins, distinct areas of enrichment at the two faces, but rather less so at the coins edge. There is also an inclusion visible which has a considerably enhanced silver content. The line scan (Plate 36) shows the enrichment more clearly.

The tin concentrations also follow the same general pattern as the previous coins despite the considerably reduced amount. Plate 37 shows one edge of the sample which has some very patchy areas of enrichment solely at the edge and faces of the coin, these extend some 50 to 100 μm into the coin. The inclusion mentioned above also has a high tin content, how much higher than the rest of the coin in shown in the line scan (Plate 38). It should also be pointed out that the tin-rich areas run right up to the surface with no depletion zone at the surface. Plate 39

shows a section of the coin slice further in from the edge which includes one of the holes drilled to extract the sample for AAS; it clearly misses all enriched zones taking a representative sample of the heart-metal of the coin.

The lead concentration is somewhat more consistent across the coin than in the previous two (Plate 40). The low bulk content is obviously the reason for this. Being only in the order of 1.60%, less lead is available to form globules of a separate phase. Nevertheless, there are areas of lower concentration scattered throughout the matrix, with larger, lead depleted areas at the coins edge and surfaces. Three small but significant lead rich inclusions also stand out as red and white features, the largest of which corresponds to the inclusion already picked out as being high in silver and tin.

The maps for nickel and arsenic (Plates 41 and 42) show limited enrichment and depletion phenomena, but again to considerable depth. The arsenic concentration is heavily depleted at one face, but enriched at the other. The nickel is generally depleted at the surface all around the exposed faces, but slightly more on one face than the other. The inclusion continues to stick out as being higher in the respective metals than the surrounding matrix. These phenomena are not a product of the samples topography. This is apparent by the fact that one element is enriched where the other is depleted. However, to provide further proof, figure 55 shows the plot of a series of point analyses (concentration against depth) for nickel.

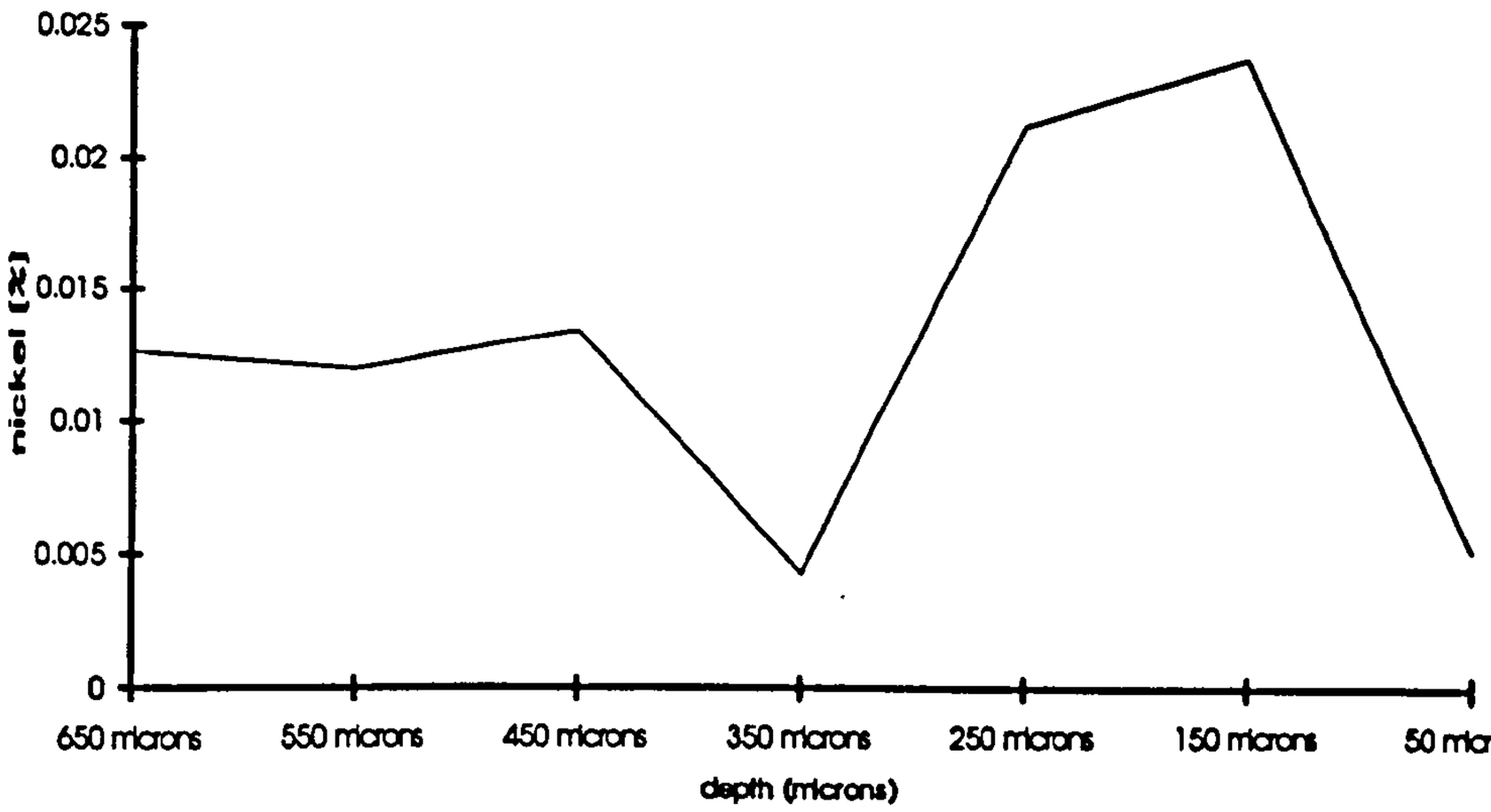

FIG. 55. PLOT OF NICKEL CONCENTRATION AGAINST DEPTH FOR SAMPLE NO.62.

This shows a clear depletion of nickel from about 150 µm beneath the surface. The same plot for tin (Fig.56) confirms the enrichment so apparent in the concentration map. Furthermore, all the points analysed were pre-selected using the secondary electron image facility and were all

located in good, clean copper-alloy matrix sufficiently distant from any inclusions or corrosion to avoid any 'excitement volume' effects.

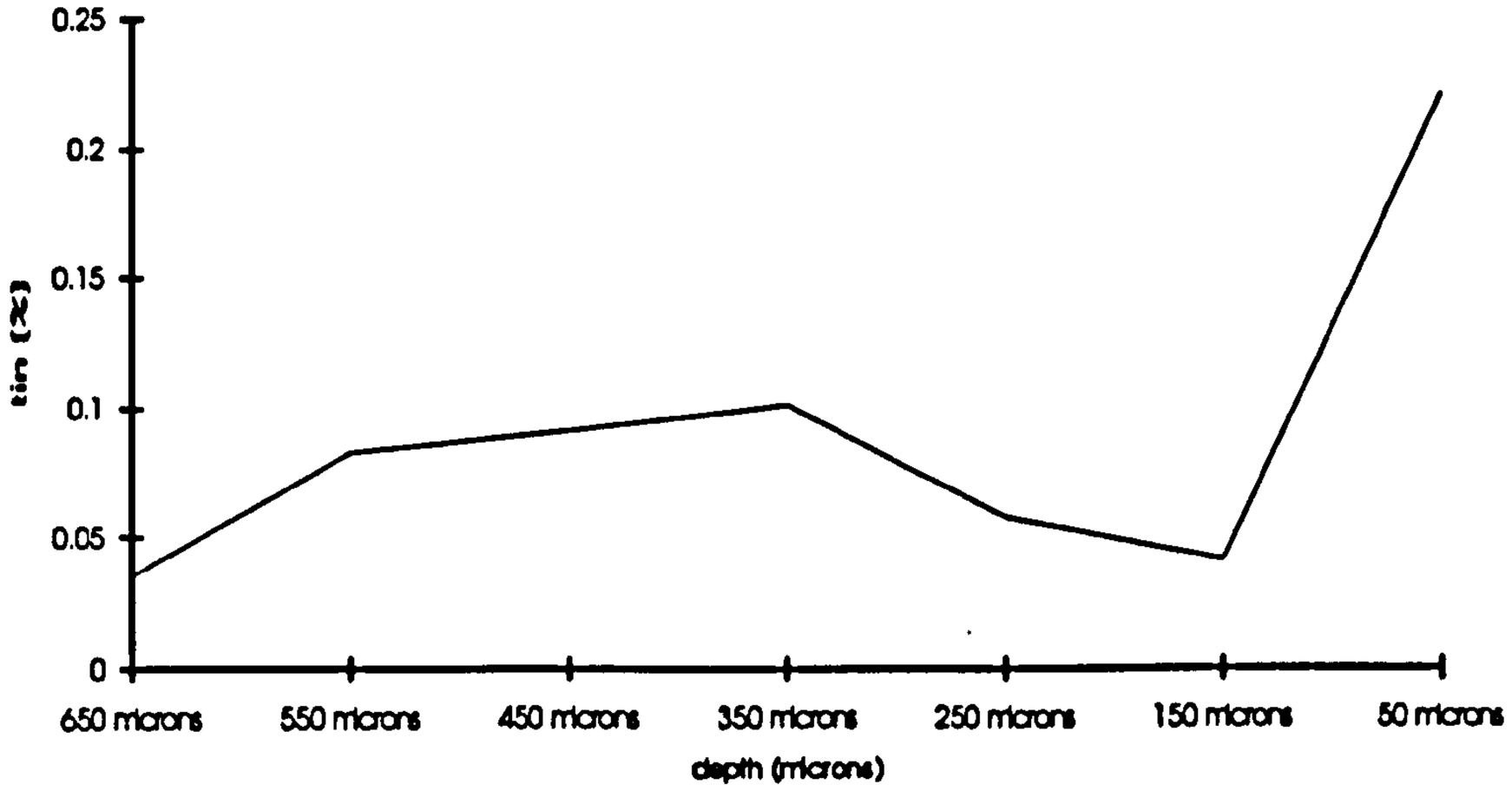

FIG.56. PLOT OF TIN CONCENTRATION AGAINST DEPTH FOR SAMPLE NO.62.

The zinc content is also low (0.028% by AAS) and its greater solubility in the copper matrix is readily apparent in Plate.43. A few small enriched areas are apparent, most notably the inclusion at the top edge, the same inclusion which is noted above. However, it is interesting that the nickel is not so evenly distributed given that, under equilibrium conditions, it is completely soluble in copper, whereas zinc has good but only partial solubility[9] . It is probable that the minute amounts of both should allow total solubility. Non-equilibrium conditions and the affinity of these elements to other elements (such as iron) which are less soluble in copper are likely explanations.

The un-etched photomicrographs (Plate 44) show part of the bottom face in the concentration map. The less vesicular structure is readily apparent, which is less prone to intergranular corrosion. As can be seen from these photomicrographs, corrosion penetration is somewhat less than was evident in the previous, more highly alloyed, coins. The silver-rich lead phase can clearly be seen, the grain size increasing towards the coins surface. These grains have also clearly been flattened by the action of striking.

The etched structures (Plates 45 and 46) again repeat the story of the previous coins; fairly large equi-axed grains, some twins, globules of lead phase distributed between. That the composition of the lead phase varies quite considerably was demonstrated in the first study, here it is possible to see a difference in colour between some of the globules. Plate 47 shows the grain

[9] Zinc has 25% solubility in copper at 210°C (Cope 1972.14).

structure at the edge of the drill hole. The grains are seriously distorted by the process, but the area drilled would clearly have comprised of material representative of the un-modified interior metal.

4.2.1.4 Study No.4; Elmer 764, radiate of Tetricus I (Sample No.68).

This coin is another product of the Gallic empire, similar to the coin in the previous study. The photomicrograph in Plate 48 shows a similar structure with relatively few voids. The AAS bulk analysis gave the following composition; silver 0.72%, tin 0.15%, zinc 0.213%, nickel 0.01%, iron 0.042%, lead 2.08% and arsenic 0.10%. Concentration mapping produced no surprises, the elements exhibit much the same trends as they have in the previous three studies and the same phase separations are apparent. The silver concentrations show a significant enrichment extending to at least 0.5 mm beneath the surface, with sporadic silver-rich points within the copper matrix. The line scan (Plate 49) compares very favourably with the multiple point analysis in figure57 below.

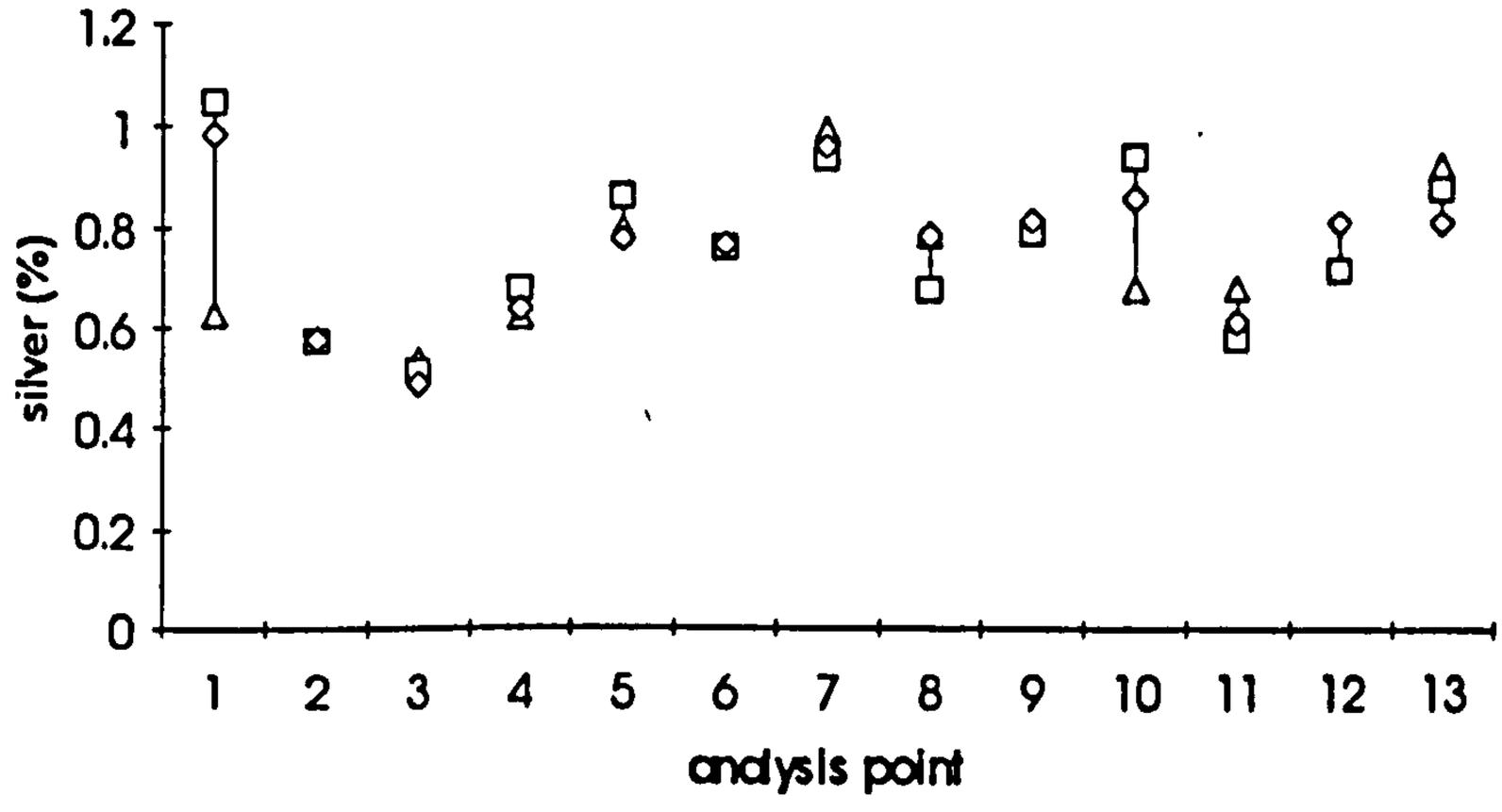

FIG. 57. PLOT OF SILVER CONCENTRATION AGAINST DEPTH (ANALYSIS POINT) FOR SAMPLE NO.68.

The plots showing the multiple point analysis have been generated in a different way for this study. Here all three separate analyses are shown for each point selected to show the degree of variability in the analysis of a single point. In general the variability is not great and is primarily caused by fluctuations in the probe current. For this reason the very first reading on a run is usually erroneous (see the first point in fig.57 above). However, it was felt appropriate to include all values in this study to demonstrate the importance of multiple analyses.

The scale has also been altered in these plots. The approximate measurement in microns has been replaced with analyses points numbered from the outside in. However, they still correspond to approximately ten micron increments.

What is interesting about the distribution of the elements and consequently of the phases, is that the 'top' of the coin is almost always richer than the 'bottom'. The same phenomena has been noted in the first study above, but it is not as marked as here. This is readily apparent in Plate 50 and is also picked up in the line scan (Plate 51). The same goes for the lead map (Plate 52). A line scan running horizontally shows little more than the lead-rich inclusion at the coins edge and the drill hole (Plate 53). A line scan running vertically across the coin into the richer zone shows a very even gradient throughout the coins section (Plate 54). This seemed far too even and convenient to be real, and it was thought that it must be topographical phenomenon resulting from the sample not being level. In order to confirm this the usual system of multiple point analyses was used. This is an independent method of line analysis which requires each point to be focused individually. This removes the potential problems caused by an altering focal distance. The results of this analysis are plotted in figure 58.

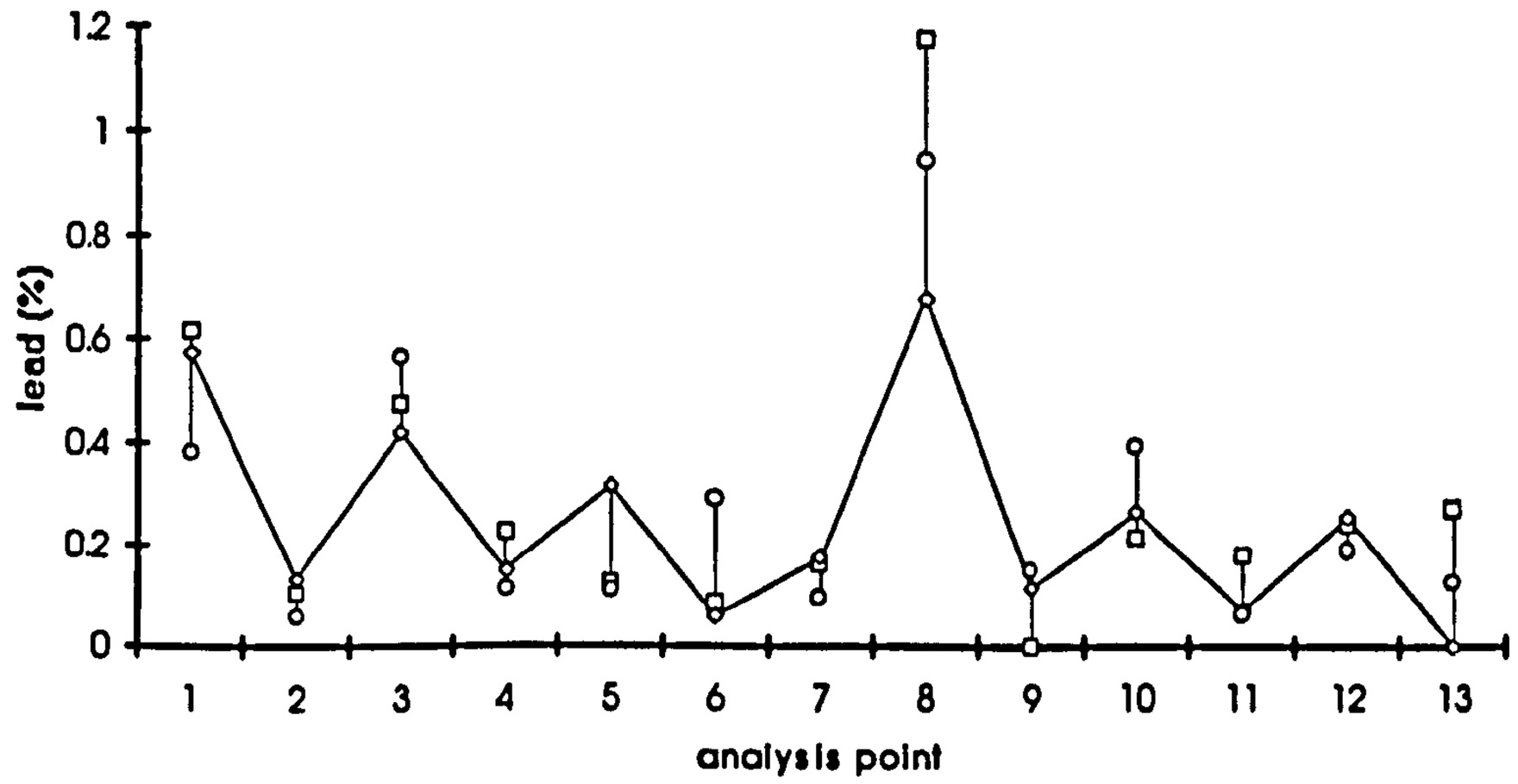

FIG.58. PLOT OF LEAD CONCENTRATION AGAINST DEPTH (ANALYSIS POINT) FOR SAMPLE NO.68.

Although less steep (due to the length of the depth scale) the same general trend is apparent in this analysis. This would suggest that the area towards the top of the coin is indeed richer in many components. This same trait is apparent to a lesser extent in both zinc and iron (Plates 55 and 56). Arsenic (Plate 57) on the other hand exhibits a generally patchy distribution with distinct globules of arsenic rich phase concentrated at the edges and both faces of the coin. This is very similar to the pattern of distribution shown by silver, and is confirmed by the multiple point analysis (Fig.59).

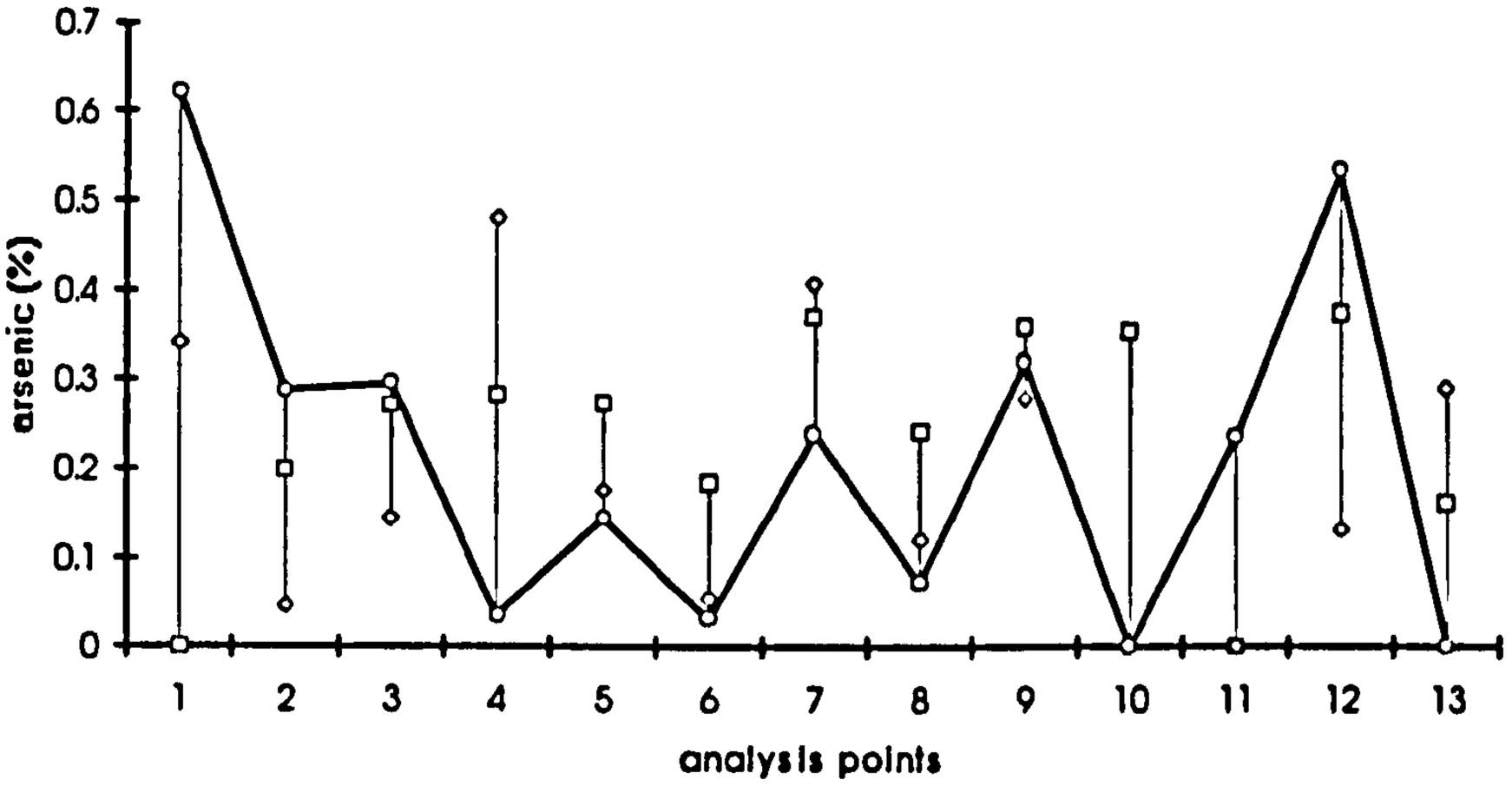

FIG 59. PLOT OF ARSENIC CONCENTRATION AGAINST DEPTH (ANALYSIS POINT) FOR SAMPLE NO.68.

The photomicrographs again show various parts of the coins structure. Plate 58 shows a globule of the lead-rich phase partly corroded out at the coins surface. Adjacent to this are smaller grains of the silver or tin rich phase, often in association with lead-rich globules. This explains the frequent similarity between the distribution patterns of the lead, tin and sometimes silver. Plate 59 is an etched (with ferric chloride) photomicrograph of part of the coins edge. It shows part of the enriched area shown in the maps as well as the grain structure of the copper matrix. The structure is again very similar to that of the coins in the previous studies; distorted equi-axed grains, some twinning, phase separation, all suggesting a similar production history.

4.2.1.5 Discussion and conclusions.

The use of the EPMA shows how severe and varied the effects of the burial environment can be and, furthermore, how closely linked these effects are to the constituents themselves. The points observed in the introduction to this section can now be explained, and further phenomena have been identified which must affect the way we perceive and interpret analyses of complex copper alloys:

1) The significant variations in the lead contents are attributable to both segregation and corrosion of a lead rich phase created by the insolubility of lead in copper. Furthermore, this effect runs deep into the surface of even relatively clean and apparently little corroded coins and will vary markedly from coin to coin. The overall amount of lead present in the coin initially will also determine the amount segregated at the surface and ultimately corroded out. The degree of segregation will also be dependent upon the cooling conditions in antiquity, and whether the coin

was hot or cold struck. If hot struck, as these were, then further segregation of the lead-rich phase will occur as this phase will almost certainly become liquid at the striking temperature.

2) The zinc contents are all very low, well below the minimum level for solubility. There is some evidence for the surface depletion of zinc (see concentration map for zinc in No.68) although the map of No.62 shows slight surface enrichment. If the zinc has a higher level of solubility in either lead, tin or silver as would seem likely judging by its distribution, then (given the electrode potentials) the zinc will be corroded out along with these elements. Furthermore, zinc compounds formed by the corrosion processes are easily diffused into the environment (Condamin and Picon 1972.63).

3) Tin is apparently depleted in the coins with a relatively high tin content, whereas the coins with a low tin content appear surface enriched. The explanation of this is again related to the amount and distribution of the lead. The affinity (due to solubility) of tin for lead is well attested (Cope 1972.275), and is demonstrated in the phase diagram in fig.60.

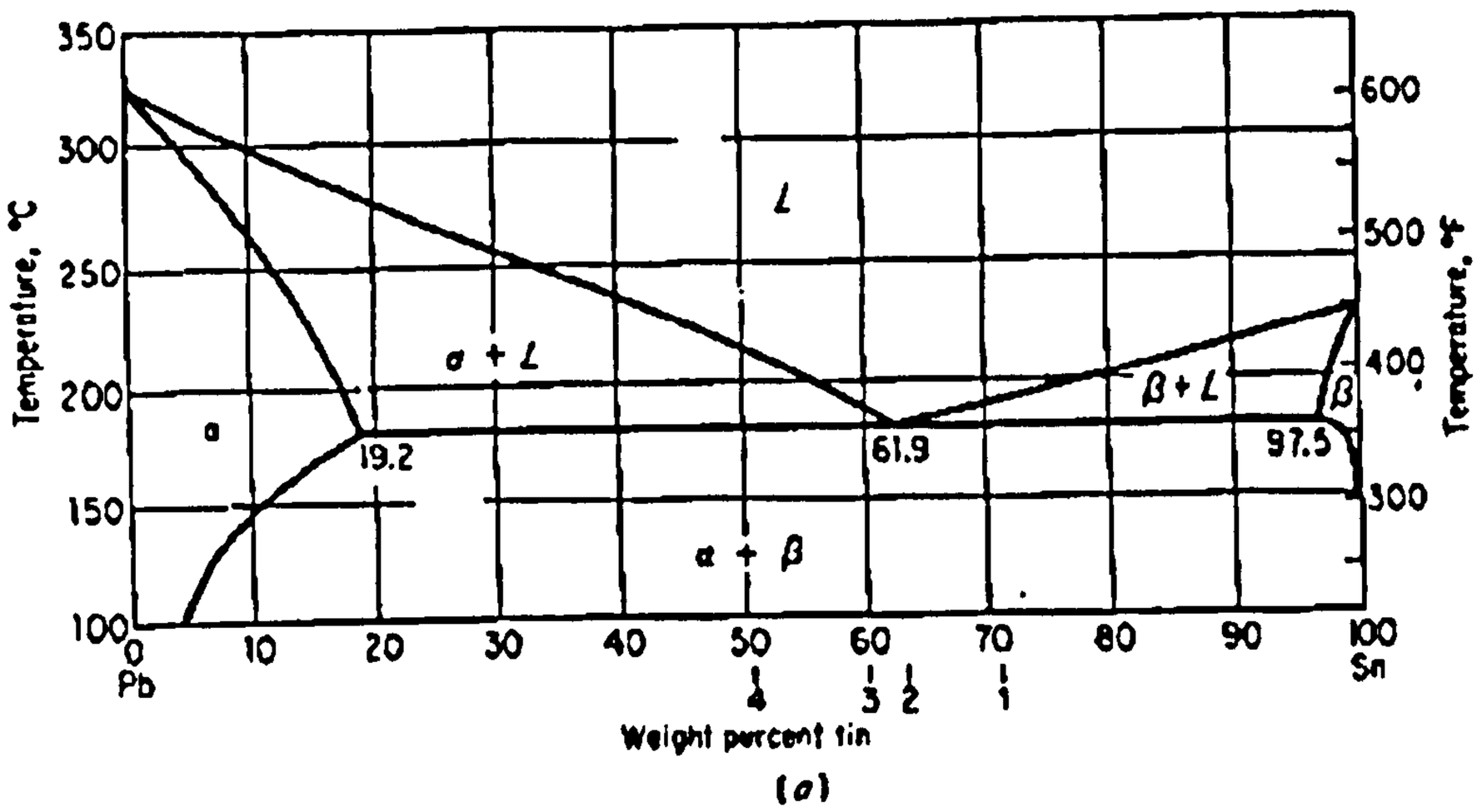

FIG 60. LEAD-TIN PHASE DIAGRAM (AFTER AVNER 1988).

It appears that a significant amount of the tin is amalgamated with the lead and undergoes the same segregation process as a consequence. The result being that where lead-rich phase globules remain within the surface layers so too do tin and other associated elements. Where this phase is preferentially corroded out so too, apparently, is the tin. However, it is also likely that the tin is merely being 'diluted' as it forms the corrosion product SnO_2. The same volume being filled by SnO_2. Furthermore, the copper lost in solution could also be replaced by excess SnO_2 resulting in an apparent depletion. Thus, the coins containing the most tin (those of Claudius II, Nos.28 and 30) are also the most highly leaded and also the issues where the XRF results are consistently lower than the AAS determination. If we refer to the tin concentration maps of Nos. 28 and 30 we see that No.28 is depleted in tin on one face and enriched in the other in an almost identical pattern to the lead. No.30 on the other hand appears to show enrichment of tin at the surface, yet

a look at the lead concentration map shows an accumulation of large lead globules is the same areas. It appears therefore that there is no rule which can be generally applied except that whatever happens to the lead-rich phase will also happen to those elements associated with it. Indeed, the electrode potentials would suggest that all the metals that appear to corrode out in the lead-rich phase are the more electronegative[10], and therefore even more prone to corrosion than the lead. If we refer to the photomicrograph (Plate 58) of the lead-rich phase at the surface of No.68, we can clearly see areas where corrosion has attacked a more electronegative secondary phase within the lead phase.

4) Silver is enriched at the surface of these coins, and to quite a considerable depth. Its electrode potential is +0.83 (Smithells 1962.1027), yet despite this a certain proportion of the silver appears to be corroded out along with the lead-rich-phase and associated metals. This lead to the appearance of a small silver depleted zone at the very surface of coin No.30. The mechanism behind this is currently unclear, but is likely to be a result of the silver being 'diluted' by oxygen, carbon, hydrogen and especially chlorine as it forms corrosion products in a similar fashion to the tin. The common ion effect is also going to play its part, the concentration of particular ions in the ground water affecting the solubility of the metal salts (Vogel 1981.23). If the silver corrosion product formed is insoluble it will obviously remain at the surface, if it is soluble then it will diffuse into the environment leaving a depleted layer.

Generally speaking, it is the behaviour of the lead which is responsible for much of the distribution patterns of the alloying components. Those elements which have a high solubility in copper at the concentrations present, such as nickel and silver, are less affected by the distribution of the lead. This is generally true of all the constituents where the concentration is within copper solubility limits, and this is obviously dependent upon the solidification history of the alloy, and can vary from coin to coin.

The amount of lead present also appears to be a significant factor. The greater the amount of lead added to the alloy, the greater the segregation. But also the greater the amount of associated elements will be which will go into solution with the lead in preference to the copper. Consequently, a highly leaded coin is likely to have a large proportion of its silver and tin in solution with the lead. If, as is again likely, there is considerable segregation of this phase at the coins surfaces and edge, then enrichment may well be apparent to some considerable depth. This effect is illustrated in plates 60 and 61, using 3-element mapping of sample N0.68 (study No.4). If, however, the coin is corroded, then this lead phase will be corroded out in preference to the copper. Some of the silver may well have been left behind at first (dependant on mobility of corrosion products), but the tin will have gone with the lead (due to almost identical electronegativity as well as solubility and mobility of corrosion products). This will have left

[10] Electrode potentials at 25°C; Lead -0.126, tin -0.136, nickel -0.25, iron -0.440 and zinc -0.762 (after Smithells 1962.1027).

voids in the copper matrix which would allow the electrolyte easy access to the coins interior and thereby increase corrosion. Furthermore, the ground water appears to bring with it an increase in the concentration of iron. This is not always the case, but certainly the maps (and multiple point analyses) of the iron concentrations within the more porous coins of Claudius II (Nos.28 and 30) showed a significant increase in iron at the surfaces and edge. The same phenomena is much less apparent in the concentration maps of the two Gallic issues, with a considerably less porous structure. Sample No.62 (plate 62) shows a fairly general scatter of iron throughout the coin, with maybe some slight enrichment at the top surface. Sample No.68 shows slightly more, most being associated with the lead, however. At the concentrations revealed by AAS analysis, iron is insoluble in both copper and lead. Therefore the presence of iron with lead, in this case, is more likely to relate to the deposition of iron from the ground water into voids left by the lead corroding out.

In conclusion, there are a variety of processes which serve to significantly alter the concentration of the different constituents within this sort of complex copper-alloy. The mechanisms are at times obscure, and only suggestions can be made based on the knowledge of metals under equilibrium conditions. What is obvious is how severe the alterations can be to the surface layers of these alloys, and also how deep into the alloy these effects can go. The coins examined in this set of studies are quite well preserved examples from a hoard, so they will have been subjected to the same burial environment. Yet each coin has reacted to that environment in a slightly different way, dependent on composition and solidification history.

From this study we see not only the reasons for the discrepancies between the AAS and XRF results discussed above, but also the problems inherant in using any surface analysis technique to analyse complex copper-alloys. Even with the preparation technique of Carter[11] , the amount of surface metal removed is clearly insufficient to allow a representative and *archaeologically* meaningful analysis. Furthermore, the inconsistency of these phenomena means that such a large area of surface would need to be removed to such a depth to gain acceptable results, that the technique could no longer be regarded as 'non-destructive'. Indeed, the author strongly believes that even Carter's (1964) standard technique for pure copper and orichalcum coins is more damaging to the coin than the drilling technique employed here.

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[11] Some of the existant literature recognises a part of these problems, yet the warnings are usually understated and ignored. In 1980 Carter and Theodory stated that,

> "Lead in relatively high quantities, sometimes presents a problem for XRF because it may be depleted for a thickness greater than 25 microns at the surface." (Carter and Theodory 1980.67).

The studies presented here demonstrate the degree of under-estimation in this statement. Furthermore, Carter himself published a set of analyses where XRF was used to analyse coins which yielded up to 6.8% lead by that technique !! (Carter 1983). The problems inherant in a data set of this type must be obvious in the light of the above discussion.

4.3 The Richborough Lump: a spatial study of compositional variation

4.3.1 Introduction.

The nature and circumstances of the discovery of the Richborough hoard IV have been discussed above (Chapter 3.2.3.1). This section is concerned with the compositional study conducted on the hoard and its findings. As mentioned above, this group offered a rare chance to investigate a hoard of coins where the individual coins are, as it were, in situ. The previous section has investigated how the concentrations of the different constituent metals within a coin ' s alloy can alter dependent on a variety of pre- and post- depositional phenomena, and how these can seriously effect any analysis which includes or analyses only the surface layers. The next logical step was to see if the compositions of coins changed relative to their position and degree of corrosion within a hoard (obviously the degree of corrosion will often be related to the coins position).

Consequently it was decided to investigate the range of compositional variation between apparently numismatically identical coins in relation to the position of each coin within the Richborough concretion. This information would also be used in conjunction with the analyses of numismatically comparable material from a relatively protected environment (Tingrith; chapter 3.2.2). This has enabled the post-depositional modification suffered by these coins to be investigated.

4.3.2 Method.

In order to accomplish this investigation it was first necessary to accurately record the relative position of each coin within the concretion in three dimensions. Various possible methods of doing this were considered; ranging in complexity from simple cardboard models up to sophisticated photogrametric imaging techniques. However, it was eventually decided to use a computer aided design (CAD) program called Microstation (Intergraph Corp.1991). This was chosen mainly because of its ability to interface directly with database programs, as well as for its relatively user-friendly interface.

Although primarily intended as a design program for architects and engineers, Microstation also has the ability to draw simple standard shapes from sets of Cartesian co-ordinates. In this case it was necessary to reduce each coin in the concretion to a set of three Cartesian co-ordinates relating to three arbitrary points along its visible edge.

To do this the Reflex Metrograph in the Department of Photogrametry, University College, London was used. This instrument is capable of accurately recording the position of a given

point in three dimensions and writing the information to disk as an ASCII file. The co-ordinates in the resultant ASCII file were then read into dBase III plus, one of the data base programs with which Microstation can be linked. A user command program was then written[12] which instructed Microstation to read the co-ordinates from the data base and use the data to draw a series of circles corresponding to the coins in the concretion, each coin being given a unique number.

This first image was unsatisfactory for two reasons. Firstly, Microstation drew precise circles to represent each coin; unfortunately the coins themselves are often far from circular. This lead to some coins being represented as either too large or too small. This problem was further complicated by the fact that the depth of the layer of corrosion products also distorted the initial measurements leading to increased inaccuracy in some parts of the image.

To minimise the effects of these phenomena it was decided to standardise the size of the coins in the image. A Microstation application command was therefore written which instructed Microstation to find every coin with a radius that was either less than 9mm or greater than 11mm and redraw it with a standard radius of 10mm. Thirty coins were re-drawn in this way, the resultant image being much more accurate and 'lifelike' (plates 63 and 64).

Once the relative coin positions in the image were as accurate as possible the concretion was carefully dismantled; each coin being bagged separately and marked with the number of its Microstation image. The dismantling of the lump was accomplished mechanically using a scalpel, and samples of the corrosion products were taken for future analyses. As each coin was removed from the concretion its position and number were carefully marked on the Microstation image in order to ensure that all the coins in the concretion had been recorded by the Metrograph.

The coins were now given a very quick mechanical clean in order to enable an exact identification against the assumption of numismatic similarity and to investigate the degree of preservation. It was rapidly apparent that the levels of corrosion differed quite considerably from area to area. Some of the coins around what, for convenience sake, we shall call the 'top-front' of the concretion were visibly more corroded than those elsewhere in the lump. The original orientation of the lump was not recoreded by the excavator (Cunliffe 1968).

Once identified the coins were then sampled by drilling in the usual fashion. The presence of differing degrees of corrosion was born out during sampling, one of the coins being totally mineralised. Others were seriously effected by inter-granular corrosion to a considerable depth,

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12 Written by Ian Wetherhogg of QA Design systems Ltd.

despite being clearly identifiable and visually relatively un-corroded beneath the corrosion products. Those coins which only had a small section of edge visible at the surface appeared less corroded, many retaining some of the white-metal coating which had covered the coins when new. This coating was usually found in the corrosion products surrounding the coins, having been lifted from the coins surface by the initial cuprite layer. This had an interesting effect with the coating of one coin adhering to the adjacent coin complete with a perfect negative image of its owner. The coins in this condition sampled well, revealing little obvious intergranular corrosion.

Once the drillings had been taken from each of the seventy-three coins the samples were analysed by AAS for the usual suite of elements. The analysis was conducted in three batches which were run consecutively. The same set of standards were employed for each batch to ensure analytical consistency. Antimony and cobalt levels were found to be to too low at the standard dilution (≡10 mg to 25 ml) to achieve the accuracy desired for this study. Consequently these two elements were run again using fresh solutions of a higher concentration (≡10 mg to 10 ml).

The results are given in the appendices, and generally appear consistent with what one should expect for these issues (see chapter 3). The first stage of data analysis has already been discussed in chapter 3, where the analyses of numismatically identical coins from the 'lump' and the Tingrith hoard were compared. The results of this are quite clear; the compositions are significantly different.

It is, of course, important to establish that there are significant differences between the compositions of the coins from the Richborough 'lump' and those numismatically identical issues from the Tingrith hoard. The PCA discussed in chapter 3 demonstrates that there are significant differences but cannot quantify them. It was decided that the best way to do this was to conduct standard t-tests (Orton 1993. pers comm.). The results are shown plotted below. Each graph shows the significance level for each element; the greater the significance level, the greater the level of similarity between the populations being compared. The size of the sample population and the fact that we are dealing with an individual experiment are sufficiently limited to allow the use of this technique without running into too many of the problems associated with the 'multiple comparison problem' (see Miller 1966). The danger is that the more elements that are compared will lead to a spurious statistical significance even if there are no 'real' differences. In order to counter this problem, specific multiple comparison techniques have been developed. However, Miller (1966.34) states that, *in the majority of instances*, data from an individual experiment of a single researcher will not require multiple comparison techniques.

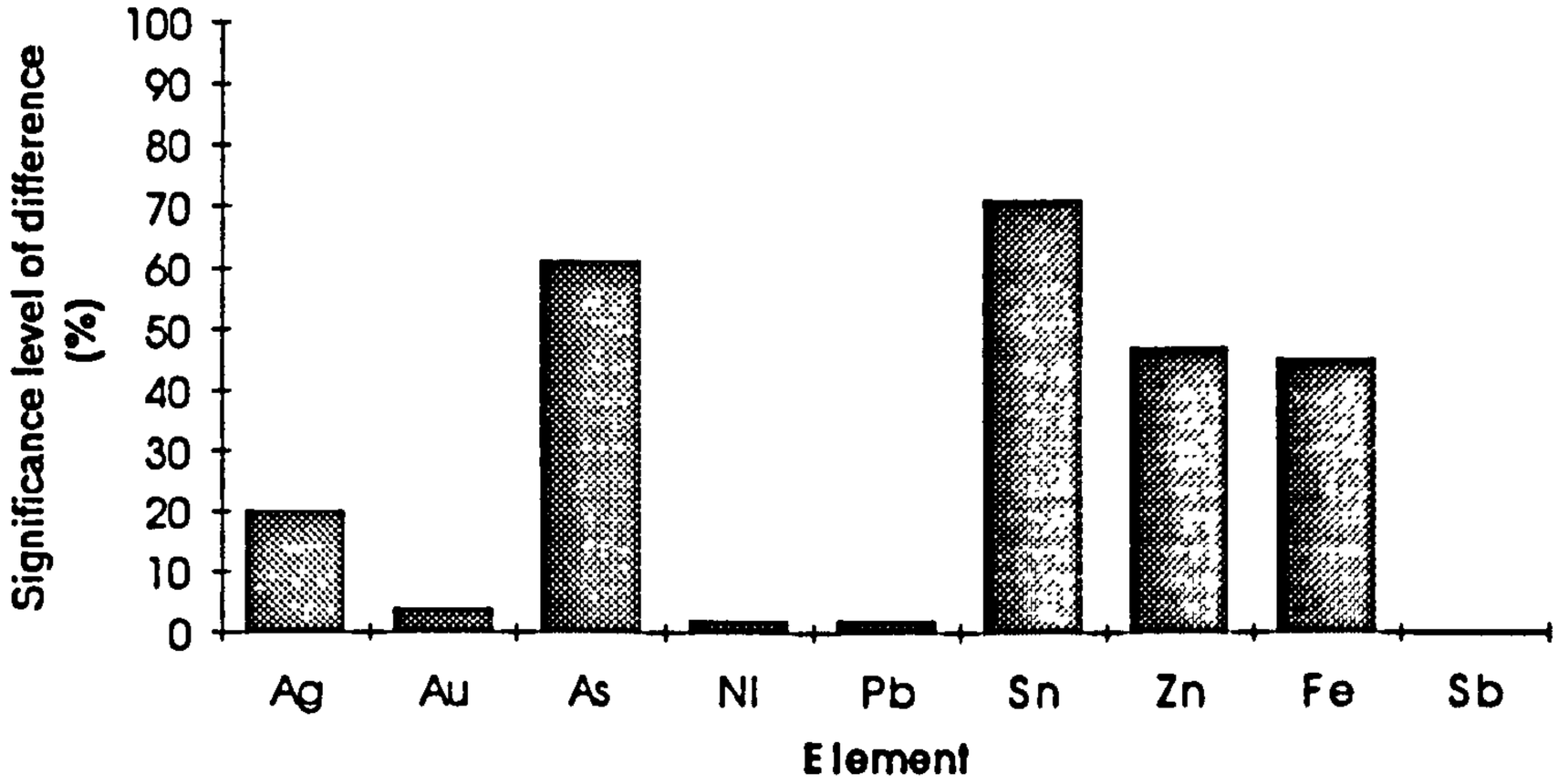

FIG 61. GRAPH COMPARING SIGNIFICANCE LEVELS OF DIFFERENCE BETWEEN BEATA TRANQUILLITAS ISSUES FROM BOTH HOARDS.

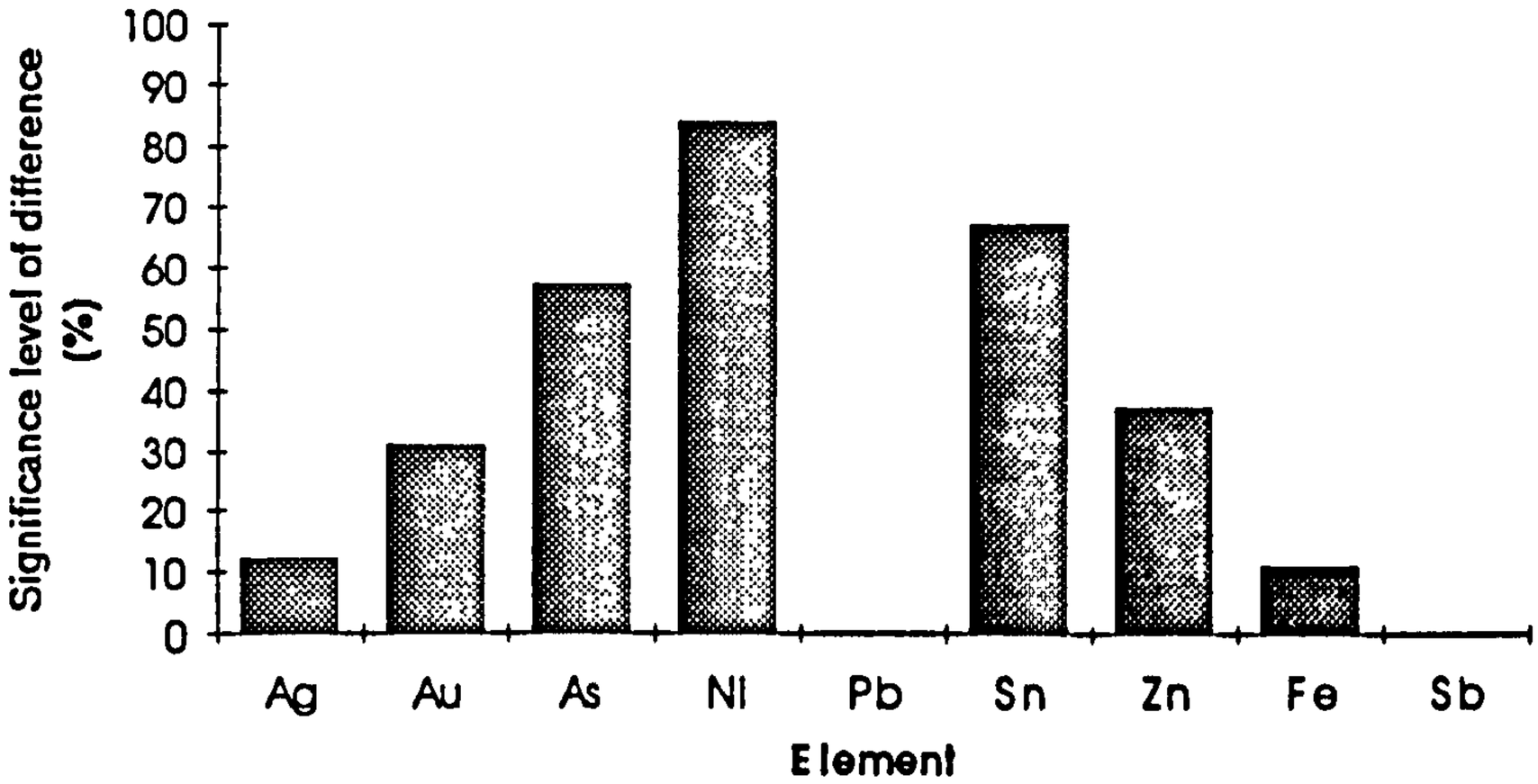

FIG 62. GRAPH COMPARING SIGNIFICANCE LEVELS OF DIFFERENCE BETWEEN CAESARUM NOSTRORUM ISSUES FROM BOTH HOARDS.

It is clear that the probability that the samples analysed from each group (Tingrith and Richborough) are similar is generally low. The greatest significance level is 84.4% for the nickel values in the Caesarum Nostrorum issues (fig 62). The mean values are close to 0.04% for each population, with 18 degrees of freedom. However, the nickel values for the Beata Tranquillitas show considerably more difference, with a significance level of only 1.8% with 17 degrees of freedom. Non of the elements exhibit important similarity (a degree of difference is inevitable given the factors discussed in chapter 2), although in both cases tin and arsenic do show more similarity than the other elements. Comparison with the results of t-tests conducted on the Tingrith analyses shows how much higher the significance levels generally are, despite the fact

that the Tingrith analyses were conducted on the two different issues (Fig 63) which would be expected to differ at least slightly.

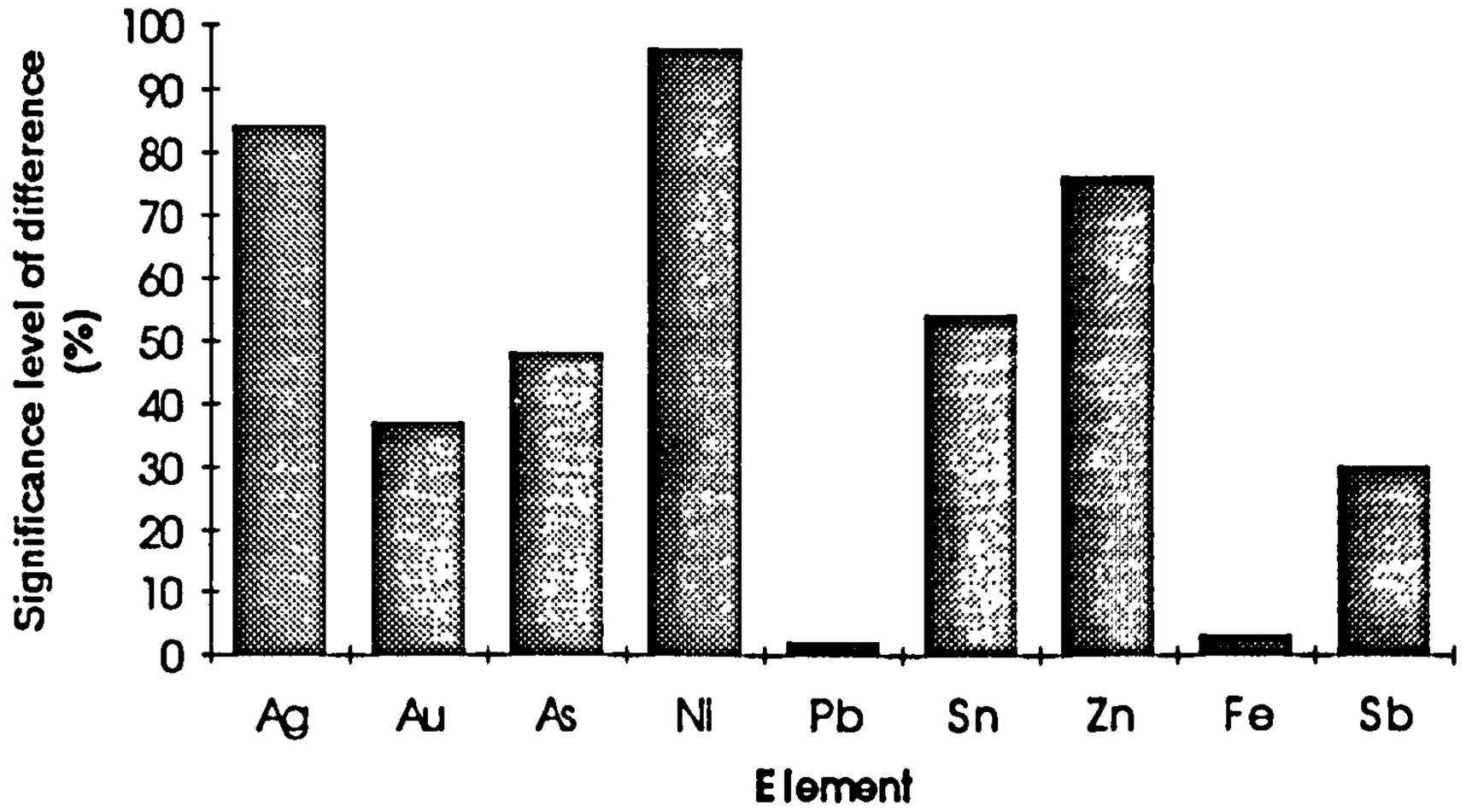

FIG 63. PLOT OF SIGNIFICANCE LEVELS OF DIFFERENCES BETWEEN THE TWO ISSUES TAKEN FROM THE TINGRITH HOARD.

As a control test, t-tests were conducted on two random sub-sets taken from the Richborough hoard alone. The results of this give even higher significance levels. These are presented in the graph in figure 64.

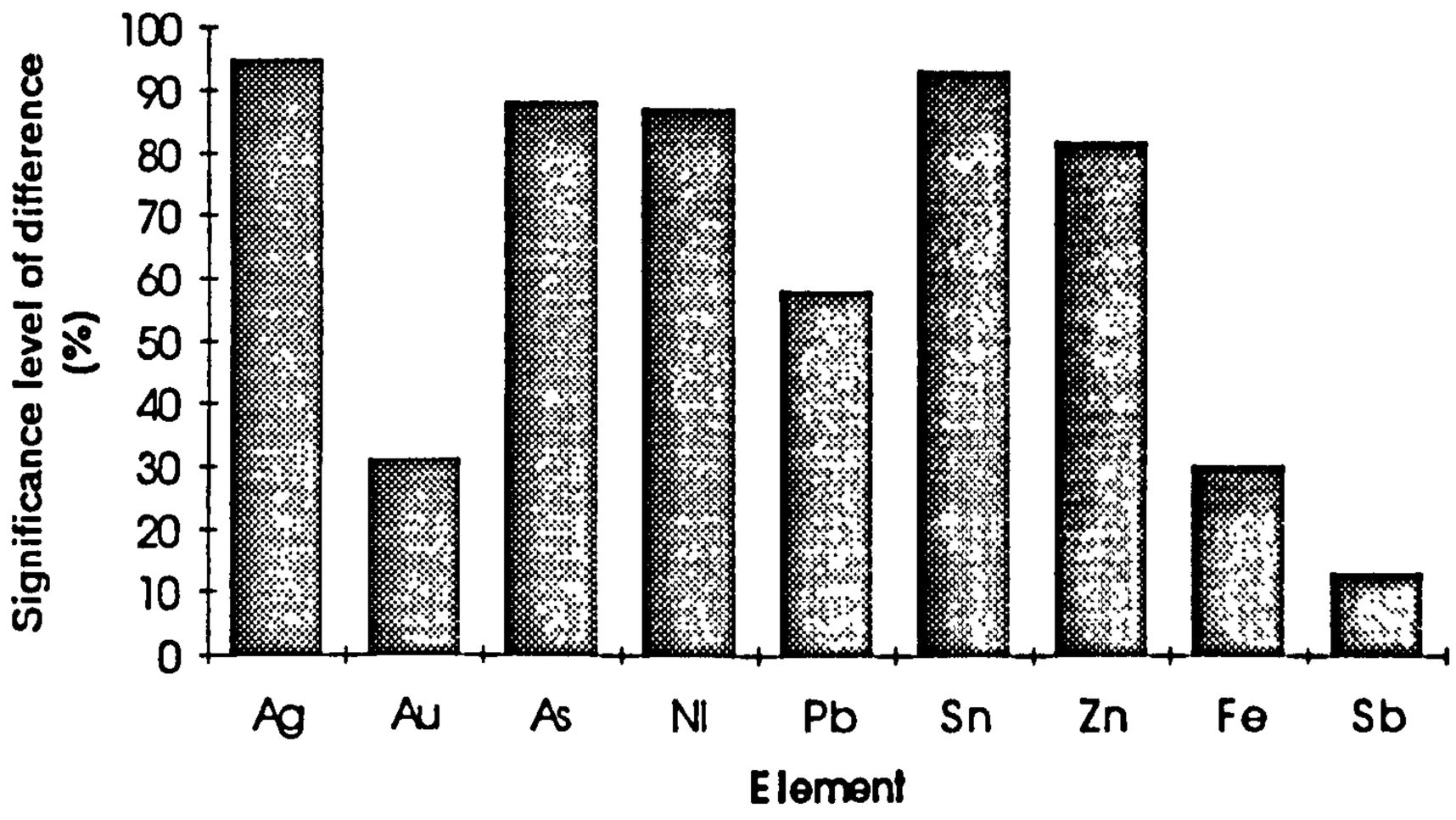

FIG 64. PLOT OF SIGNIFICANCE LEVELS OF DIFFERENCES BETWEEN RANDOM DATA SETS TAKEN FROM THE RICHBOROUGH HOARD.

The spread of values is very similar to the plot of significance levels derived from a data set of purely random numbers (fig.65). This is what was expected, the two groups randomly selected from the Richborough hoard are very similar, that variation which does appear is all random.

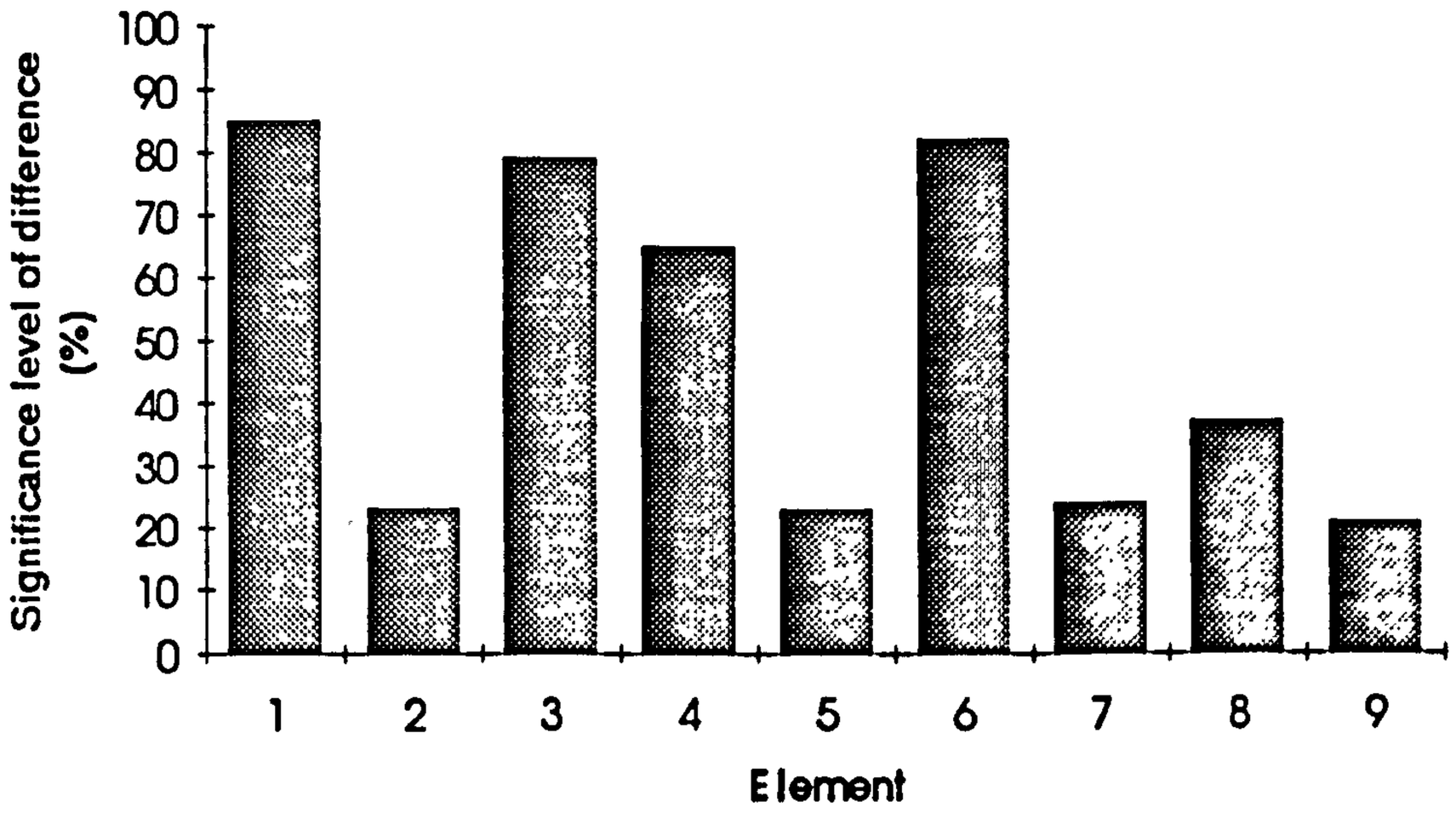

FIG 65. PLOT OF SIGNIFICANCE LEVELS OF DIFFERENCES BETWEEN RANDOM DATA SETS .

With this as our 'base-line' we are better equipped to judge the spread of values from the previous tests. The two Tingrith groups do show significant differences in their iron, antimony, lead and gold contents. However, identical issues exhibit significant differences when coins are compared which are from the two hoards. At this level, the Beata Tranquillitas issues differ significantly in their antimony, iron, zinc, lead, nickel, gold and silver contents. The Caesarum Nostrorum issues differ on exactly the same selection of elements excepting nickel. In other words, both sets of analyses conducted on the coins from the Tingrith hoard differ from the analyses of numismatically similar material from the Richborough hoard in an almost identical fashion.

The lead, not surprisingly, shows very little similarity either between issues or between groups. A plot of randomly selected analyses clearly shows the consistency of the differences between the lead contents of the two groups across the same issues.

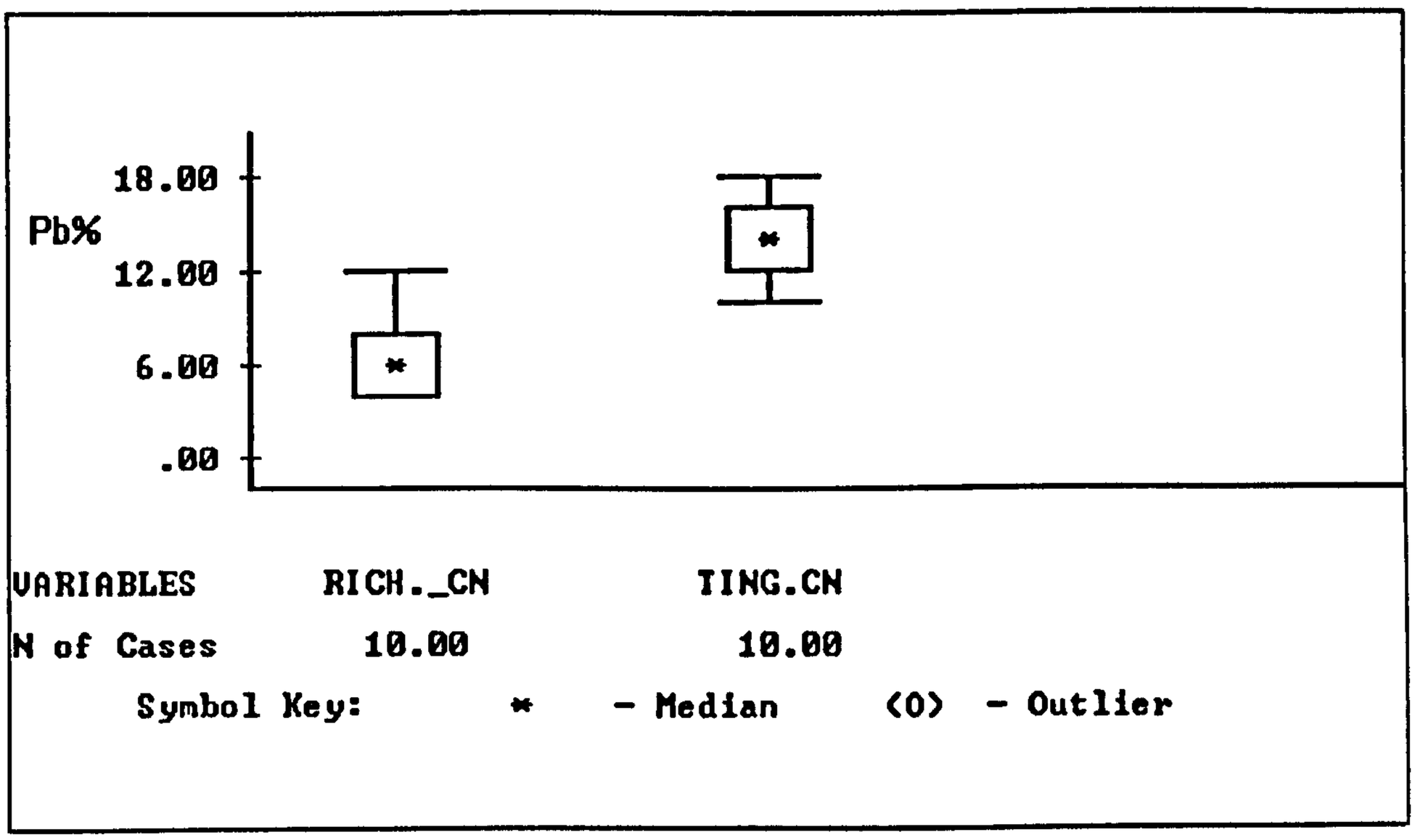

FIG 66. LEAD CONTENT OF CAESARUM NOSTRORUM ISSUES OF TRIER (RIC 441)

Generally speaking the differences between the compositions of the coins selected from the Richborough group and the Tingrith hoard are significant. Not one element shows a value which is significant at higher than the 85% level. It therefore seems reasonable to reject the hypothesis that the results from the two groups are equal.

The next stage consisted of adding the analytical data to the database linked to the Microstation image. Once this was done it became possible to select any coin in the image (by using the mouse), and then calling up a database screen showing all the compositional details of that coin (plate 65). By the same token, it is also possible to use Microstation to search for a particular coin, and colour it a chosen colour.

More importantly, by running standard database queries and writing the results to a separate database, such as 'all coins with a silver content of greater than 0.7%', it is possible to get Microstation to colour all the coins in the query database a given colour, and then rotate the image to study the positions of the coins. This was done, the results forming the following section.

4.3.3 Results.

As a first stage the analytical data were subjected to a principal component analysis (PCA), log-transforming the data first and excluding the copper values to circumvent the unit-sum constraint problem (see chapter two). The plot using all included elements (fig 67) shows a large central cluster with a second cluster towards the top and a further two small clusters at some distance from the main group.

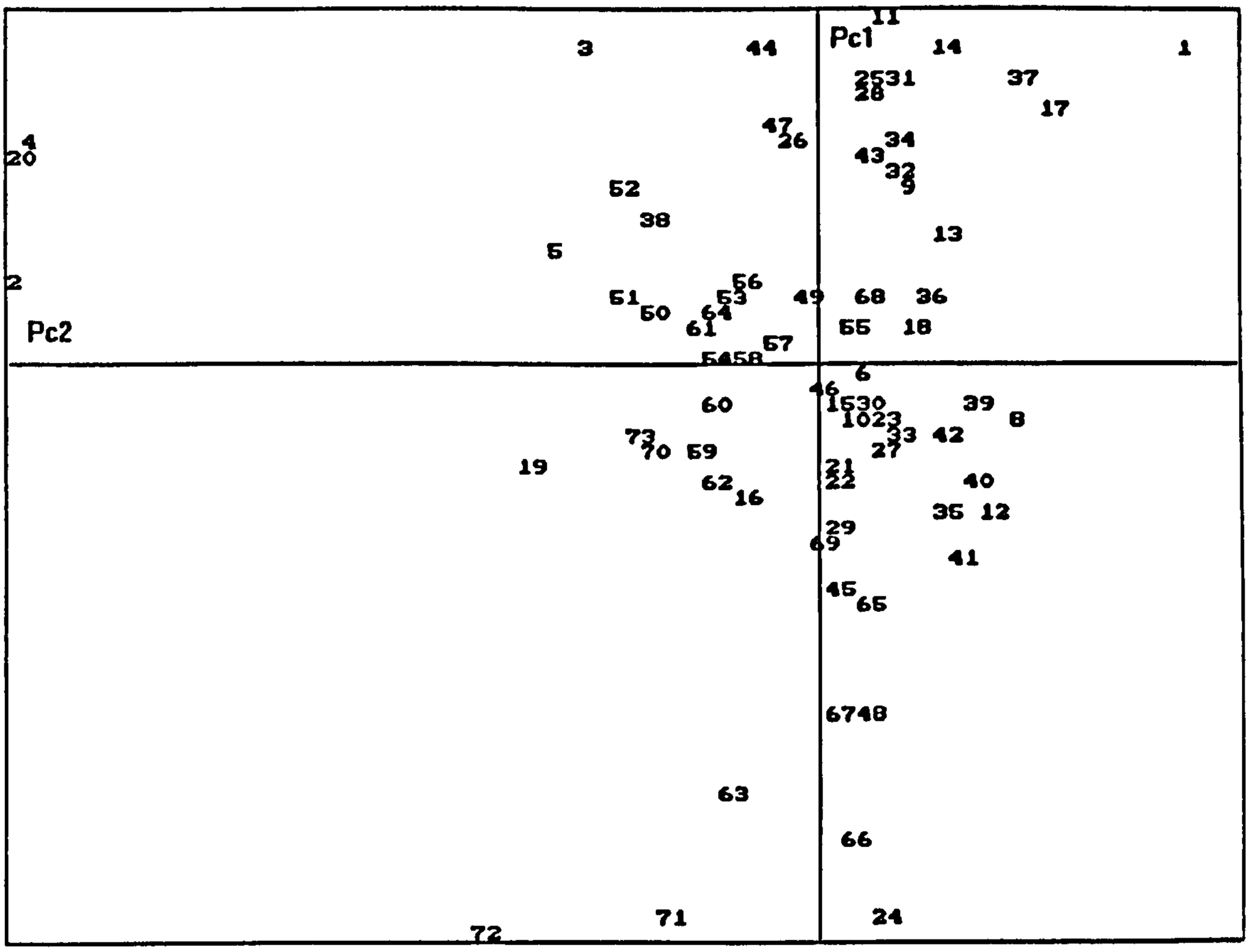

FIG 67. PCA PLOT OF ALL RICHBOROUGH HOARD DATA (NUMBERS REFER TO ORDER ONLY).

The variable loadings show that iron is responsible for the most variation on the second principal component (0.87), together with zinc (0.19). The most important contributor to the first principal component is gold (0.83), however, this is due to one outlier with an abnormally high gold content (No.1). PCA of major and minor components did little to add to the picture, although lead was by far the most variable metal of the three major components (silver, tin and lead). Removing the iron from an all elements re-run produced a tighter cluster with a scatter of outsiders orbiting around it. It also supplied a further set of elements showing significant variation which had previously been obscured by the greater variability of iron. These elements were lead, tin and zinc, perhaps unsurprisingly. Two other elements showed lesser, but still significant variability, arsenic and antimony.

Consequently, using this data, a PCA was first run using only those elements showing the greatest variability; iron, lead, tin and zinc. The resultant plot is shown in fig 68 below.

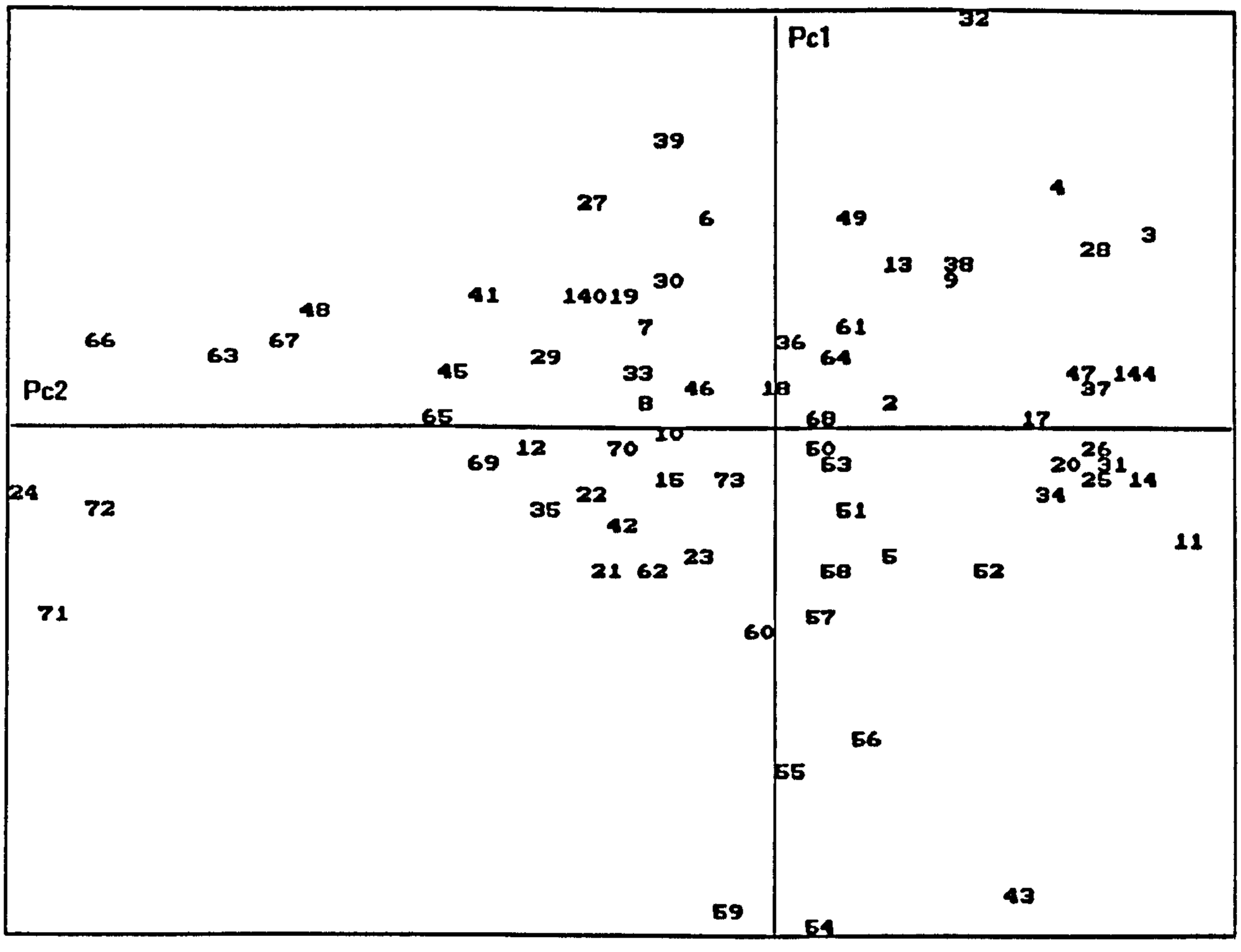

FIG 68. PCA PLOT OF ELEMENTS SHOWING MOST VARIABILITY (NUMBERS REFER TO ORDER ONLY)

Again, no discrete clusters are apparent, but groupings are definitely there. To the bottom and to the left and right of the plot are the most convincing clusters. Iron is responsible for most of the variability on the first principal component, with lead and zinc contributing most to the second.

Having produced a PCA plot which identifies those coins whose most variable components are showing even greater variation, it was necessary to see if there was any pattern in their location. To do this a new database was constructed consisting of only the thirty-one coins picked out by the PCA as being in some way different. This was then linked to the image and Microstation was then instructed to identify the location of these coins by colouring them red. The result is shown in plates 66, 67 and 68. The 'top' view (plate 66) shows that the coins separated by the PCA are also quite distinctly grouped spatially. Rotating the image to show the 'right' side of the concretion shows this group continuing down this side, as it also does to the left (plate 68). Thus the coins picked out by the PCA also form quite a distinct group located along the top-front of the concretion and continuing over its right and left ends.

However, this group is based on a combination of elements, not on any one particular metal. The next stage was to investigate the behaviour of the individual elements. To do this it was

decided to first look at the frequency histograms for each element. This showed that three of the elements had bimodal distributions (Shennan 1988.39). In other words that the iron, lead and arsenic values each contained two normal distributions, one main and one subsidiary, which would suggest two distinct groups behaving differently.

Consequently each of the elements showing a bimodal distribution had a separate database created for it containing the details of those coins which fell in the subsidiary peak in the frequency histogram. This database was then connected to Microstation and those coins in this secondary database were picked out in the chosen colour. However, the bulk of the elements all produced normal distributions suggesting that any concentration gradients within the lump were going to be very subtle. The task of deciding which value was significant as the top (or bottom) of the 'normal' variation parameters was very difficult. The obvious starting point was the analyses of the comparative material from the Tingrith hoard. Generally a figure was chosen corresponding to the mean value for that element in the Tingrith coins. All coins with values of either above or below this figure, depending on their chemistry, were then regarded as of interest. This data, coupled with the information in the frequency histograms of the Richborough analyses, enabled some tentative figures to be suggested. Once this point had been decided upon Microstation was told to locate those coins in question and show where within the lump they were located.

4.3.3.1 Iron.

Iron was one of the three elements possessing a bimodal distribution. Consequently, this fact coupled with the data from the Tingrith material suggested that looking at the position of the coins with an iron content of over 0.3% may be useful. The resultant image is shown in plates 69, 70 and 71. The set of four tiled images in plate 69 give a general idea of the distribution. Most of the coins containing over 0.3% iron are located in the top-right area, with a few of the coins at the surface on the front also having a high iron content. Plates 70 and 71 are enlargements of the top and front views to show this effect more clearly.

4.3.3.2 Silver.

Silver showed a normal distribution, with four outliers of over 1.25%. The most frequent value was 0.7% (close to the Tingrith mean of 0.67%), and the distribution of coins with silver contents over this (44 coins) appears fairly random (plate 72). If the image is inverted to show coins with a silver content of less than 0.7%, we get the image shown in plate 73. This, oddly perhaps, shows more patterning. The center appears to contain most of the coins with lower silver contents, however, a few of those coins whose face was totally exposed at the surface were also found to be depleted in silver.

Taking a lower silver value of 0.59% we see that the distribution of the coins containing less than this amount is predominantly at the surface (plate 74). Although by no means all coins at the surface fall into this group. The picture is further complicated by the fact that some coins are half inside and half at the surface of the lump. It is very likely that the composition will vary within a coin dependent on which part was totally exposed or within the concretion. Nevertheless, it appears that most of the coins possessing silver contents at the lower end of the scale are to be found towards the surface and particularly at the back of the concretion.

4.3.3.3 Lead.

The lead values have a bimodal distribution with peaks at about 5% lead and then at 10% lead. The majority of coins fall between 3% and 7% lead (74%). Only about 10% of the coins form the subsidiary peak. Extreme values are held by Nos.20, 36 and 72. The first concentration limit to be looked at was 5%. Plate 75 shows the location of the coins with a lead content of less than 5%. A degree of regionality is again evident, especially in the isometric view (view 2). Rotating this view slightly shows a more convincing image (plate 76), with more coins with a lower lead content appearing at what is the bottom left of the image. To try to clarify this feature further a lower concentration limit of 4% was chosen and those coins with a lead content equal to or less than this were picked out (plate 77). The same trends are apparent, but the regionality is more pronounced. In particular the band running from the right of the front view round to the right view and then up to the top view is very clear.

4.3.3.4 Zinc.

The zinc values are normally distributed over a very tight range. There are two slight outliers (Nos. 36 and 44) which are on the high side. However, all values are low, the maximum being 0.152%. Consequently, expecting a certain amount of de-zincification, a concentration limit of 0.03% was chosen, and coins with a zinc content equal or less than this were located. The results of this are shown in plate 78. The sixteen coins which conform to this concentration band are all quite tightly grouped, with one outlier towards the right - bottom. The remainder are concentrated at the top - front of the lump.

The maximum value for the zinc in the Richborough material is closer to the mean for the Tingrith coins (0.09%). This supports the suggestion of de-zincification, those coins picked out by this analysis being the most severely effected.

4.3.3.5 Tin.

The tin values are again normally distributed between 0.8% and 5.8%. Extremes are both high (No.45 at 5.8%) and low (Nos.61 and 67 at 0.8% and 1.1%). De-stannification of the coins in the more corroded areas was the working hypothesis, so it was the coins with lower than 'normal' tin contents which were of interest. An upper limit of 2% was chosen on the basis of the

Tingrith study (mean of 3.5%) and the frequency table. The results are shown in plate 79. Only twelve coins conformed to this criterion. However, there is a notable overlap between these de-stannified areas and those which are de-zincified. This strongly supports the hypothesis that the phenomenon is a function of the level of corrosion as it relates to position. These interelationships will be discussed fully below.

4.3.3.6 Nickel.

The nickel values conform to a normal distribution with five extreme values (No.63 at 0.1%, No.24 at 0.8%, No.67 at 0.88%, No.61 at 0.67% and No.80 at 0.65%). A value of 0.04% was selected as the lower limit, and all coins with higher values than this were investigated (this includes the extreme values). The twenty coins which conformed to this criteria have a distribution not dissimilar from that of the lead, and there is, indeed, some overlap with both the zinc and tin distributions (plate 80). The regionality is, as with the lead, not limited to a specific area, but rather a number of smaller, yet discrete, areas.

4.3.3.7 Gold.

Gold is also normally distributed. There are six extreme values at either end of the scale (No.1 at 0.39%, No.9, 15 and 43 at 0.08%, No.13, 14 and 19 at 0.07%). A value of 0.046% was chosen as the lower limit with all coins having a gold content greater than this being picked out (this includes the upper extremes). The resultant image is shown in plates 81 and 82. The mean value for the Tingrith coins was 0.04%.

The marked regionality is surprising given the minute amounts of gold present. However, the enrichment of the gold content in the coins shown does form a distinct pattern. The Top - Back area and its patchy continuation down the back is readily apparent. Closer inspection reveals that there is a central core of non-depleted coins running from top to bottom. This is best seen in the back view, where both top and bottom un-depleted coins are visible, with the central core partially obscured by some of the outer coins. There are also some interesting comparisons with the other metals; some overlap with iron and silver but a marked degree of mutual exclusivity with lead, zinc and tin.

4.3.3.8 Arsenic.

Arsenic is the third element to exhibit a bimodal distribution. The main peak is responsible for about 52% of the coins, the subsidiary about 20%. There is only one extreme case, No.21 at 0.66%. Consequently, on the basis of the frequency plots, a lower limit of 0.279% was chosen, with all coins having an arsenic content greater than that being shown (including the outlier). The regionality in readily apparent in the image (plates 83 and 84). There is also notable correspondence between those areas enriched in arsenic and those areas enriched in silver, but depleted in lead.

4.3.3.9 Antimony.

The antimony values are normally distributed, although there are ten extreme values (No.61 at 0.250%, No.30 at 0.170%, No.1 at 0.100%, No.33 at 0.109%, No.46 at 0.108%, No.74 at 0.110%, No.5, No.20 and No.8 at 0.020% and No.23 at 0.030%.). A lower limit of 0.075% was chosen on the basis of the Tingrith material and the frequency plot, with all coins having an antimony content greater than this being selected. The resultant image (plates 85 and 86) again shows remarkable regionality given the minute amounts of antimony present. Nineteen coins matched the given criteria including six extreme values. The distribution of the antimony rich coins only appears to overlap to any degree with the silver enriched areas. However, those areas which appear enriched in gold and nickel are not enriched in antimony, whereas those with lower concentrations of iron and lead are also not high in antimony.

4.3.4 Discussion.

This study demonstrates how the level of exposure to an aggressive burial environment can seriously effect the individual composition of otherwise numismatically and compositionally similar coins. The variation picked up in this analysis is not due to experimental variability between the three separate AAS batches. This was checked using t-tests. The coins appearing in the different concentration zones are from all three batches. Furthermore, the rigorous employment of standard reference materials and standard solutions minimised instrumental drift or other error.

The extent to which even the trace elements are affected is alarming. Obviously, the degree to which a given element is prone to either enrichment or depletion is dependent upon the chemical factors already discussed in chapter 2. The nobility of gold, for example, will go some way towards explaining why such minute amounts of the metal are subject to such a strong distribution pattern. However, other factors, such as the presence of certain ions (common ion effect) in the ground-water, will also effect the degree of 'solubility' of a metal salt in the ground-water (Vogel 1981.23) and , as a consequence of this, its mobility. These are complex factors, the extent of which can only be guessed at; many changes being undergone over the passage of time. Yet it remains a fact that the observable changes which do take place can introduce a significant error into the analysis of an archaeological artifact.

The interrelationships between the different metals present another interesting story. The initial visual assesment of the Microstation images exposed some basic trends. The coins enriched in both silver and arsenic only occur beneath the surface layers, whereas those coins which are either enriched in silver or in arsenic appear only at the surface. This would suggest that the coins at the surface are individually possessed of higher than normal silver or arsenic

contents, and that the depleted coins at the surface are more indicative of the norm. Likewise, the coins within the lump appear enriched, but are merely not depleted. This observation, of course, fits in with what one would expect in these circumstances. Furthermore, despite the rigerous sampling proceedure, it may be that those coins retaining part of their silver coating may have had their sample contaminated by it.

There seems to be little obvious relationship between the distribution of coins depleted in iron and those enriched or depleted in silver. Where there is some notable overlap is between silver and iron enriched coins at the top surface of the lump. This would be in keeping with the hypothesis that the iron content can be strongly related to the degree of corrosion. The increase in iron being the result of iron leaching into the coins matrix from the ground-water during corrosion (see section 4.2). There also appears to be no relationship between iron and gold, presumably for similar reasons.

The silver depleted areas and the gold enriched areas appear to overlap to a limited extent. This may suggest that the gold contents in this case are correlated with the silver. This is not surprising given the likelihood of the gold being a trace impurity in the silver added to the alloy. The distribution of the gold has already been mentioned above. The existance of the enriched central core running through the lump from its top to its bottom is, on the face of it, perplexing. The chemical nature of gold precludes the formation of corrosion products and therefore any mobility within the lump. However, the fact that most of the enriched coins appear concentrated at the top and bottom of the core would suggest that this is, after all, predominantly a surface phenomona. This can then be explained in terms of standard electrochemestry, with the more noble component being left behind and consequently appearing enriched after its less noble bed-fellows have been taken into solution and formed corrosion products. This interpretation is further supported by the observation that there is some overlap between the silver depleted areas and the gold enriched areas.

The strongest and most consistent overlaps are between the coins depleted in lead, tin and zinc. This is to be expected given the segregation phenomena discussed in the previous section. The significant variable here would be the lead, taking the other two elements into solution with it. The greater electronegativity of the zinc and the mobility of its corrosion products would contribute to its preferential corrosion, followed by the tin and lead (which share similar electropotentials and less mobile salts). Consequently the areas which appear depleted in these metals are also those most heavily corroded, and are also almost exclusively at the surface of the lump. There is also a significant overlap between those coins depleted in lead and those enriched in silver. This is particularily true of those coins at the surface of the lump. The suggested

mechanism here is again simple; the silver seems enriched due to the preferential corrosion of the copper, the lead being depleted because it is corroded in preference to both silver and copper.

The correlation between the areas visibly suffering from corrosion, the areas suggested by the principal component analysis as being 'different' and the areas shown by the concentration of individual metals to be significantly different, is indisputable. The 'top-front' area of the concretion was the most visibly corroded. The coins distinguished by the PCA also came from this area. Furthermore, approximately the same area was responsible for those coins depleted in lead, zinc and tin and enriched in iron, nickel, arsenic and antimony.

The silver distribution is more complex to explain probably due to the interference of the silver coating. Generally most of the coins having low silver contents are at the very surface of the concretion and at the back. This suggests that it is both those coins which are very heavily corroded and those which are not greatly corroded which have silver contents below the 0.7% level chosen. This fits in well with the assumed corrosion models. The highly corroded coins would have lost much of their silver (and other metals) and those coins suffering from 'moderate' corrosion would appear enriched in silver due to the preferential removal of some of copper.

As a general rule, the constituent elements behave as their chemistry would suggest. Furthermore, the behaviour patterns identified on the micro-scale by the EPMA in the previous section are also apparent here. There are, inevitably, some differences, but the overall trends remain. It appears that silver and tin can be both enriched and depleted at the surface dependent on the degree of corrosion undergone, and the amount of lead present. The radiate coins used in the EPMA study containing over 1% tin showed depletion at the surface, whereas those containing less than 1% showed enrichment. This would agree with the depletion seen on the macro scale here, with the mean tin content being 3.45%. The silver shows both enrichment and depletion in both studies and for a number of different reasons pertaining to both the alloy and the environment. The gold and antimony appears enriched at the surface of individual coins and in those coins in the more corroded areas of the hoard. The only element which shows depletion at the surface of individual coins and enrichment in those coins in corroded areas in the hoard is arsenic. Both the studies discussed above and the work published by Gilmore (1989.365) show arsenic severely depleted at the surfaces of individual coins, yet the distribution coin by coin within the hoard clearly shows that the corroded areas are enriched in arsenic. This may well reflect the degree of localised corrosion at the surface of the coins.

The iron concentration appears in both studies to be strongly influenced by the degree of corrosion. Both at the surface of coins which appear relatively free from corrosion and in the bulk analysis of coins which are obviously heavily corroded. The fact that iron appears to leach

into the copper-alloy is a complication not previously reported in the study of archaeological metal. The effects of this on the normalised analytical results from standard WD-XRF are obvious, and introduces yet another level of inaccuracy.

The variation in the effects of the corrosion processes cannot be over-emphasised. There are many factors which can have a role to play and which can have vastly different results. This study demonstrates how dangerously misleading the analysis of corroded material can be, even if the material all comes from the same source and appears relatively free from corrosion. The necessity of multiple analyses is also evident.

4.4 Problems relating to the accurate quantification of silver in archaeological copper-alloys by atomic absorption spectroscopy.

During the course of the analytical programme it was suggested by WD-XRF, conducted at the British Museum Research Laboratories, that the silver content of the Fenny Stratford blanks (Chapter 3.1) was really in the order of 0.9%, and not 0.4% as the initial AAS analyses indicated. This discrepancy was double-checked by the British Museum Research Laboratories, the results indicating that further investigation was required. The reason for this significant error was initially thought to be unrecognised precipitation of some of the silver as silver chloride during the dissolution of the sample in aqua regia. The usual way round this is to adopt a method using two solutions, one using very low sample weights and high acidity using aqua regia, the other using more sample (10 mg+) and high acidity using only nitric acid (Hughes et al. 1976.27). However, it was found that significant differences occurred in the absorbence levels dependant on any one or combination of the following factors;

1) *Very slight* differences in the acidity between standard and sample.

2) Use of only *nitric acid* to make up standards, especially if sample is dissolved in aqua regia.

3) *Age* of both standards and sample if in *nitric acid* only.

4) Presence or absence of *copper* in both sample and standard.

Although the need to match standards and samples closely to prevent inconsistencies caused by different matrices has been known for some time (Hughes et al.1976), the significance of the differences between aqua regia and the 'going off' of both samples and standards when in nitric acid only seems not to appear in the archaeological science literature.

The main article in the scientific literature concerning silver determination by AAS (Belcher et al. 1964) reports that there is no interference in the detection of <10 ppm of silver by Co, Cr, Cu, Fe, Ni, Pb, Sn, Zn or Au and other metal nitrates (Belcher et al. 1964.1258). Furthermore no interference was noted using hydrochloric or nitric acids, although a reduction in absorbance caused by increased viscosity was noticed when using sulphuric or phosphoric acids (Belcher et al. 1964.1258).

To try to unravel this situation, three separate 50 ml solutions containing 4 ppm of standard silver solution were made up each acidified by 6 ml of acid. One used conc. HCl, one conc. HNO_3 and one aqua regia (1:3). Initially, when the solutions were fresh, close agreement was obtained in the absorbance levels for each solution (0.271, 0.230 and 0.253 respectively), however, after the first hour the absorbance of the solution acidified with only conc. HNO_3 had

fallen significantly (0.201) and repeated readings taken during the following three hours showed a dramatic fall off (0.102 and 0.093). Both the solutions in HCl and aqua regia gave consistent readings over this period.

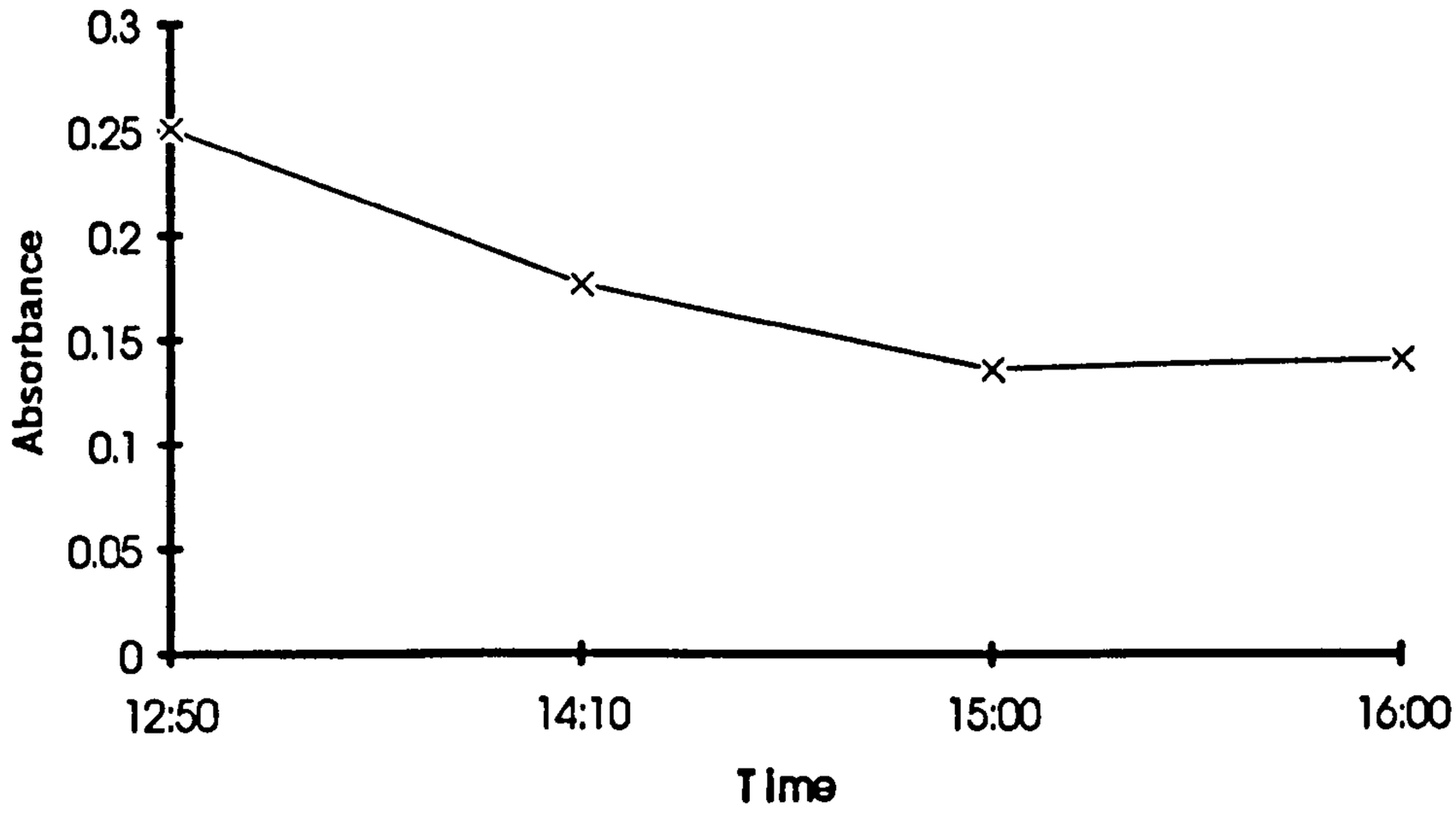

FIG 69. PLOT SHOWING DECREASE IN ABSORBANCE OVER TIME

Exactly what is happening to the silver to cause this phenomenon is unclear at present, but investigation is continuing. One initial suggestion was that some of the silver was being absorbed into the glass of the volumetric flask. This was checked by making two identical standard solutions and storing one in a glass volumetric flask and the other in a plastic vessel. No appreciable differences were noticed in the expected fall-off of absorbance between the two solutions. Another possibility is the effect of light on the photosensitive $AgNO_3$.

It was decided to test a number of permutations (repeatedly) to try to understand the range of the problem. The results are tabulated below (all in ppm);

Standard solutions used for calibration.

	4ppm/HNO_3	**4ppm/HCl**	**4ppm/Aqua.Regia**
4ppm/HNO_3	**3.83**	3.68	1.90
4ppm/HCl	5.74	**3.96**	4.22
4ppm/Aqua.Regia	5.81	3.72	**3.98**

It can be seen from this that the most satisfactory result was running a sample in aqua regia against a standard also in the *same* acid concentrations, as recommended in all texts on the subject. The sample in only nitric acid run against a standard in aqua regia gave less than half the correct result, whereas the sample in aqua regia against the standard in nitric acid gave a result of almost two-thirds greater than the true value.

Why these problems were not reported by Belcher et al. (1964) can apparently only be ascribed to differences in proce dure and possibly equipment. The Pye Unicam spectrophotometer used by both the author and the British Museum Research Laboratories uses an air/acetylene flame operating at 2400°K, the Hilger and Watts Uvispek (H700) used by Belcher et al. used an air/propane flame operating at 2100°K (Vogel 1981.815). The greater sensitivity of the higher temperature flame must be responsible for fewer interferences and serves to underline the necessity for rigorous and frequent reassessment of analytical procedures. Indeed, Kolthoff et al. (1971) in their manual of quantitative chemical analysis, whilst maintaining that AAS is less effected by flame temperature than other spectrochemical techniques, warns that;

> "...the temperature of the sample (in the flame) would be of no consequence if it were high enough to decompose all compounds *completely* into atoms, but not so high as to cause appreciable ionisation. In fact, not all compounds are completely dissociated in any source that is now used. Moreover, the extent of dissociation naturally depends upon the anion. For this reason it is still necessary, even in atomic absorption analysis, to maintain a reasonable control over the temperature and composition of the sample." (Kolthoff 1971.1002).

The inevitable conclusion of this study demonstrates that both sample and standard solutions in aqua regia are required for the accurate determination of minor amounts of silver in copper-alloys. Yet the problem remains as to how to maintain all the silver, tin and gold in solution at the same time. The two solution method was developed specifically for silver alloys where the amount of silver quantified is such that the effects noted here are insignificant. It is only at around the 4 to 8 ppm level that this effect is sufficient to cause serious problems. This means that the determination of low concentrations of silver in slightly corroded samples dissolved solely in nitric acid, run against standards in an identical matrix, will result in significantly erroneous results, as the table above demonstrates. Obviously one way around this is to reduce the sample weight to such an extent that the silver concentration is within the solubility parameters of the normal hydrochloric acid concentration of the aqua regia, however, this will inevitably seriously reduce the concentration of all elements analysed, and subsequently the sensitivity of the analysis. It was found by the author that the most satisfactory way around this problem was to maintain the sample weight at the usual level (10 to 20 mgs) and to add an extra 2 mls of hydrochloric acid to the aqua regia in both the samples and the standards. This maintains all the elements in solution, including the amounts of silver encountered in the argentiferous copper coinage alloys in question. However, this method does not get around the fact that the silver will gradually come out of solution over time, albeit not as quickly as in nitric acid alone. It was found that even solutions kept in opaque plastic bottles in a refrigerator became useless within a few days. Consequently, all silver determinations reported herein were carried out within one day of the solutions being made up, with the standards being fresh on the day used.

4.5 Comparison of wet chemical analyses and AAS analysis of Constantinian Nummi.

The most exhaustive study of the composition of roman copper-alloy remains that undertaken by L.Cope, most of which formed his doctoral thesis submitted in 1974. These analyses were standard wet chemical procedures as discussed in chapter 1, and were conducted with as much accuracy as the techniques can allow. AAS, on the other hand, allows greater accuracy for most elements whilst this accuracy is less dependent on the analyst than traditional volumetric and gravimetric techniques. The sampling strategies employed by Cope have been discussed above (chapter 2) and are open to criticism on a number of levels. Nevertheless, Copes analyses remain the most frequently cited compositional data in numismatic works. It was therefore felt appropriate to try to gauge the appropriateness of Copes technique in the light of the research presented here.

The remaining halves of the coins analysed by Cope are held by the British Museum and the Keeper of the Department of coins and medals allowed five of these to be selected and samples taken by drilling in the usual way. The coins chosen were all Constantinian issues, of similar types to the coins analysed from the Tingrith and Bancroft Villa hoards. The results are shown, compared with Copes original analyses in table 16.

	BM276	BM291	BM290	LHC7	BM59
Ag/AAS	1.74	0.99	1.21	1.04	1.17
Ag/Cope	2.00	1.72	1.70	1.76	1.84
Sn/AAS	2.34	2.20	4.24	3.37	0.10
Sn/Cope	n/a	n/a	n/a	3.09	0.31
Pb/AAS	3.94	3.56	6.49	5.27	2.70
Pb/Cope	n/a	n/a	n/a	n/a	1.86
Fe/AAS	0.01	0.01	0.01	0.01	0.13
Fe/Cope	n/a	n/a	n/a	n/a	0.42
Ni/AAS	0.05	0.07	0.03	0.03	0.02
Ni/Cope	n/a	n/a	n/a	n/a	0.03
Zn/AAS	0.02	0.04	0.05	0.05	0.04
Zn/Cope	n/a	n/a	n/a	n/a	0.01

TABLE 16. COMPARISON OF AAS ANALYSES OF COINS PREVIOUSLY ANALYSED BY COPE.

(n/a = not analysed)

As can be seen from the table, the majority of the coins were only analysed for their silver content, with only one coin receiving anything like a complete analysis. Furthermore, three of the silver determinations were by NAA, two by wet chemistry. Despite this, all of Copes silver concentrations are significantly higher than the AAS results. The reasons for this in the light of the foregoing sections are straight forward; the NAA will yield falsely high results for both technical reasons previously discussed and because the enriched zone is included in the analysis (despite the surface being 'filed'). Furthermore, all these coins would have been silver coated when new and although now no visible trace remains, it is likely that the surface would have been silver enriched by this as well[13]. The wet chemical results would be affected by the same phenomena, the most influential being the depth of the enriched zone. It is perhaps significant that the coins which show the greatest difference between silver values were initially analysed by Cope using NAA, and the smallest difference between silver determined by wet chemistry and AAS.

Only the last two coins (LHC7 and BM59) were analysed for other elements. The tin content of the coin with a low value is lower when analysed by AAS, whereas the tin content of the coin with over 1% is higher by AAS. This phenomena is remarkably consistent with the findings of the EPMA (Chapter 4.2.1.5), and would support the view that Copes sampling method includes part of the modified surface layers. Likewise the zinc level is higher by AAS than by wet chemistry, and the iron is lower by a significant 0.29%. The lead is also higher by AAS (by 0.84% or about 50% more). All these discrepancies collectively point to the inclusion of at least part of the modified surface layers and add up to an erroneous analysis.

The condition of the coins is also of interest. The report sheets for each coin include a brief visual assessment of condition which range from "corroded all over" (LHC7) to "slight wear" (BM59). However, examination by the author concluded that all the coins showed signs of being chemically cleaned in some way, a factor which is also likely to alter the composition to a significant depth.

The suggestions here are not faulting the quality of Copes' analyses, but rather the assumptions made in the sampling strategy. The quality of the analytical techniques is not in question. Indeed, the results published by Cope provided the first realistic survey of Roman copper-alloy coin compositions ever, and the results still provide a general idea about the levels of the major components used. However, the varied and un-reported sources of the material coupled with the assumptions made in sampling, make the use of his data for detailed and statistical study

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[13] Cope argues convincingly for a silvering process involving dipping the coin blanks in moltern silver chloride (horn silver or kerargyrite). This would chemically replace the copper, lead and tin at the surface of the coin with silver, and has been successfully replicated (Cope 1972.275). The other possible method is the 'sweating' out of a silver-rich lead phase immediately prior to striking (as suggested in Chapter 2). Both these processes would result in silver enrichement to a significant depth by themselves, and would be enhanced considerably by corrosion and/or agressive cleaning.

at best unreliable. Indeed, the levels of 'fineness' ascribed to these coinages by the numismatists are differentiated by differences of less than those now ascribable to surface enrichment (Tyler 1972.251).

4.6 EPMA investigations of the hoard vessels.

4.6.1 Introduction

The role of the ground-water (electrolyte) in the process of corrosion has been discussed in theory above, and the effects on the coins themselves have been studied in detail. Furthermore, because much of the material analysed for this study came from hoards that had been buried within ceramic containers, the assertion has been made that these coins are less aggressively corroded. Certainly as far a visible comparison goes, the coins from these hoards are consistently less corroded than similar material from sites (such as Market Deeping) or from hoards not buried in a container (the Richborough lump). The AAS analyses bears this fact out. However, to what extent the burial within a vessel preserves the 'original' composition of the alloy buried inside presents interesting questions.

Caley (1964.11) conducted an experiment where a copper-alloy coin was first mechanically cleaned of all surface corrosion products, weighed, and then suspended in a solution of 1:1 nitric acid. After *five minutes* the coin was removed, washed (the washings added to the solution), and both the coin and the solution analysed gravimetrically. The results are given in table 17.

Metal	Solution (%)	Coin (%)	Difference (%)
Cu	93.55	92.47	1.08
Ag	1.16	2.93	1.77
Au	none	0.03	0.03
Sn	1.67	2.52	0.85
Pb	1.15	1.79	0.64
Fe	0.25	0.05	0.20
Ni	0.07	0.05	0.02
Co	0.16	0.03	0.13
Zn	0.04	0.01	0.03
Total	98.05	99.88	
Non-metals by difference	1.95	0.12	1.83

TABLE 17. COMPOSITION OF COIN AND SOLUTION (AFTER CALEY 1964.11)

It can be seen that most of the component metals are taken into solution to a greater or lesser extent. The marked differences between the concentrations in the coin and in the solution demonstrate the selective nature of corrosion or aggressive cleaning. Furthermore, it also shows in a relative way the extent to which the constituent metals can be taken into an aggressive solution. Although the solution was designed to show the effects of chemical cleaning on a coin, the exercise works well for an acidic ground-water, especially considering that this experiment was conducted over five minutes and not centuries. The effects of a considerably less acidic solution over archaeological time are likely to be similar.

4.6.2 Method and results

To investigate this further it was decided to look at the fabrics of the vessels that the hoards had been buried in. Initially the Tingrith vessel was studied. As mentioned above (Chapter 3) the find came from a sandy environment which is aggressively acidic and iron rich. One of the sherds from the vessel was selected and a slice removed for analysis. A preliminary investigation showed the fabric to be a coarse ware with shell inclusions ('opening material' or 'temper'). This had been clearly dissolved out by the acidic ground-water at the outside face, but appeared intact on the inside. The inside face was also stained green and this green zone extended several millimetres into the vessel wall. Furthermore, it seemed that the green zone and the zone where the shell inclusions had been dissolved were mutually exclusive.

ED-XRF analyses were then carried out on four separate areas along an imaginary line from the inside to the outside face of the slice. A preliminary quantitative analysis of both the inside and outside surfaces of the sherd detected the presence of aluminium, silica, phosphorus, lead, sulphur, potassium, calcium, iron and copper. On this basis each of the four areas were semi-quantitatively analysed for those elements. The results are shown in table 18 below.

	1-Inside	2	3	4-Outside
Al	24.694	27.161	27.956	28.692
Si	34.774	43.878	46.985	48.934
P	0.576	n/d	n/d	n/d
S	0.870	0.385	0.500	0.414
K	2.265	2.902	3.138	3.501
Ca	15.101	11.294	7.574	2.612
Fe	5.660	7.014	8.458	14.594
Cu	12.762	6.835	3.534	0.761
Pb	3.325	0.567	1.893	0.501

TABLE 18. ED-XRF ANALYSES OF TINGRITH CERAMIC VESSEL

The values are all normalised, so they should be treated as approximate, the presence of light elements such as oxygen not being detected. Even so some interesting concentration gradients can be discerned. Of particular interest is the inverse relationship between the copper and the iron, a phenomenon also noted in the EPMA analyses of the Walbottle coins (chapter 4.2). The lead also appears to also be concentrated on the inside, as are sulphur, calcium and phosphorus. The outside has higher concentrations of aluminium, silica, potassium as well as iron. The gradients are quite clear for all elements, and the concentration maps[14] show this to be a general trend. Plate 87 shows the back-scattered electron image of about one third of the slice. The inside surface is to the left, the outside surface to the right. The voids left by the acidic removal of the shell inclusions can clearly be seen. This is confirmed in plate 88 which shows the calcium distribution. The inside 1500 μm or so is much higher in calcium and the zone not attacked by the acid ground-water is very discrete. Plate 89 shows the copper distribution which is concentrated in a band about 1000 μm in from the inside surface. This coincides with the interface between the acid leached zone and the acid free zone. The lead on the other hand is clearly concentrated at the inside surface, gradually lessening after about 1000 μm (plate 90). The final picture, plate 91, shows the iron distribution. This is clearly concentrated at the outside surface, but doesn't lessen significantly until it reaches the interface with the copper, lead and calcium rich zone.

A similar slice was taken from one of the Fenny Stratford hoard vessels, and concentration maps were made on the Jeol microprobe at the Institute of Archaeology in London. The inside surface of the vessel is at the bottom of the photographs. As mentioned in the introduction to the case study, the vessel is of BB2 ware, a hard fired, sandy fabric which is iron rich. Consequently the distribution of the iron appears fairly regular (plate 92). The lead, on the other hand, is clearly concentrated at the inside surface (plate 93), and the copper likewise (plate 94). The large voids are sand particles. The less porous, hard fired nature of the vessel is apparent from the limited penetration of the copper and lead.

4.6.3 Discussion

The action of the ground water in removing and redistributing significant amounts of metal due to reconstructive corrosion processes (the relative quantity being dependent on changeable chemical factors) is well demonstrated in these studies. The metals detected in these studies correspond to the two elements making up the bulk of the alloy buried in each, and would therefore have the greatest presence in the ground water. This is not to say, of course, that other metals are not present at levels below the EDAX detection limits. Indeed, Caley's (1964) experiment would suggest that most constituent metals are likely to be present. The levels of the

14 These concentration maps were produced on the Cameca electron micro-probe at the Research Laboratory for Archaeology and the History of Art, Oxford.

different components leached by the ground water will inevitably be dependent upon its nature (both components and concentration), the solubility of metal ions being greatly affected by the ion content of the ground water.

Furthermore, the effectiveness of the ceramic vessels in preventing the leaching out of these elements into the general soil matrix is not entirely clear. That the ground water within the vessel also leaches metal from the coins is apparent, and consistent with the EPMA studies of the Walbottle coins. However, it would seem that the ground-water within the vessel remains in part local to the hoard, the ceramic vessel being an effective barrier to outside leaching beyond the vessel. This would support the view that hoard material from within ceramic vessels is likely to be less severely altered by the burial environment, and that analyses of such material is likely to yield results somewhat more representative of the 'original' alloy composition.

Chapter Five:
Conclusions: meaning and application.

"There is no finishing position since there can never be any way of evaluating whether the 'right' interpretation has been arrived at...But better and better accomodations and new insights can be achieved in a continuous process of interpretation" (Hodder 1986.155)

5.1 Introduction

The ultimate aim of any program of archaeometallurgical investigation must be to enhance our understanding of the society or culture which produced the artefact/s under scrutiny. It is to this end that all discussion of phase-separations, electrode potentials and other esoterica must be aimed. This project has demonstrated how these 'esoterica' can create a maze through which the archaeometallurgist must navigate in order to gain the data needed to illuminate this small corner of the archaeological jig-saw. Furthermore, it has underlined the importance of the interpretative process in making the vital connection between the data and the archaeology. The importance of a comprehensive understanding of both the behaviour of the alloy itself and also of the limitations of the analytical techniques employed has been shown to be of paramount importance in a better interpretation of archaeometallurgical data. The application of a methodology which takes these factors into consideration has been used to investigate a set of specific numismatic and archaeological questions. Furthermore, the programme of analyses has demonstrated the severity of the effects of the corrosion processes on complex copper-alloys, and how this can lead to biased analytical results and interpretations.

5.2 Discussion of results from the numismatic standpoint.

This project has focused on the endemic copies found in Roman-Britain and dated to the period between the middle of the third century and the middle of the fourth century AD. The value of a program of compositional analyses conducted on carefully selected material has been clearly demonstrated, and the relevance of this to the numismatics and archaeology will be discussed below.

The use of elemental profiles to distinguish between officially produced coins and their copies was first demonstrated by King (1978). However, this important study was not followed up despite other studies on different material which further demonstrated the value of this approach to numismatic studies (see Carradice and Cowell.1987, for example). This project has developed Kings approach and applied it to all three major periods of copying, greatly increasing the precision and sensitivity and being cognisant of the problems inherent in sampling at all levels. It has also demonstrated that the groupings obtained through statistical analyses of minor/trace elements are not always demonstrably a function of the 'original' alloy.

5.2.1 The radiate period.

The analysis of the sample taken from the Walbottle hoard was primarily designed to supply rigorously controlled full analyses of official radiate issues to compare with the radiate copies from within the sample itself, as well as from the other groups analysed. The fact that the official radiate issues themselves showed clear compositional variability dependent upon mint and issue was an unexpected bonus.

The clear division of the official issues into products of the central empire and products of the Gallic empire has not been reported before, and lends itself to interesting interpretation. The fact that these groups are mutually exclusive indicates that the metal for each was drawn from very different sources. Furthermore, this fact also suggests that neither issuing authority was calling in and re-using the issues of the other (at least not at a level sufficiently high to effect the composition of individual coins). This may indicate that both authorities required the mints under their jurisdiction to use freshly smelted metal and not rely on re-cycled scrap. This raises the question of the metal resources available to the Gallic empire. Figures calculated on the basis of die links suggest that the numbers of 'official' radiates produced was in the order of one million coins every day (Burnett 1987.123). This is a remarkable output for two mints at the most, and would require some 24 tons of alloy every day. The differences in trace element profile indicate that the Gallic sources were independent of the sources used by the Central empire. Consequently, we must be looking at metal produced from ores mined within the area controlled by the Gallic empire. Even assuming that certain *Gallic* issues would be called in and re-issued periodically (therefore preserving the uniqueness of the elemental profile), the amount of metal required must have been huge. If the demand for freshly smelted metal was large enough to put strain on the producers, then it is possible that the value of the metal would be enhanced. If this were the case then a reduction in silver content and/or weight need not be seen as a debasement. This hypothesis refers only to the value of freshly smelted 'black copper'. The supply pool of re-cycled and previously alloyed copper-alloy would not be affected as it was not part of the coinage alloy supply cycle. The recognition of a number of different types of copper is attested in Diocletian's price edict of 301. In this, admittedly later, document three types of copper are listed with prices of 75, 60 and 50 denarii per libra, and one further type has an indecipherable price (Cope 1977b.223).

The radiate copies were the main object of this section, and have yielded important results. The analysis of the Fenny Stratford hoard alone poses some interesting archaeological and numismatic questions, calling into question some of the established views. The main point is the existence of two very different alloys where previously three different stages in the production of coins from the *same* alloy had been postulated. Furthermore, the fact that the levels of those

components which the producers would have been aware of appear to have been carefully maintained across a probable three melts of alloy is remarkable.

The production technology has also been investigated by metallography, and it is important to note that the two clearly different compositions of the blanks/pre-blanks and the pellets also have totally different production systems. The blanks/pre-blanks are of an argentiferous gunmetal containing approx.1.4% zinc and 1% silver; these were cast individually and then hammered out, some being joined together, presumably to maintain a certain broad weight standard. The pellets, on the other hand, are of a leaded high tin bronze (13%+ tin). These were produced by cutting off short lengths from a cast rod of metal, the brittleness of the alloy making the process easier. Although no examples were found in the group, other finds, such as North Leigh (Knight 1984) and Sprotbrough (Mattingly and Dolby 1982) show that the pellets were in all likelihood destined to have been hammered out into coin blanks and then struck. This automatically poses a number of questions. Davies (1988) suggests from hoard evidence that radiate copies gradually become smaller over the period of production, yet in the Fenny Stratford group we have both large blanks and the material for producing the smallest type of minim. What is represented here? Certainly the dies found would have been more suitable for striking the larger blanks. The situation is further complicated by the fact that the compositions are so different. The initial interpretation of the find had been to suggest that the pellets were to have been melted down, cast into pre-blanks and then hammered out into the blanks themselves. This was clearly not the case. It seems as if we have two types of copy represented here. It could be argued that the pellets would have been mixed with other metal not represented in the hoard to produce a similar alloy to the blanks/pre-blanks, yet why then go to the trouble of casting rods and then cutting off such small lengths? not to mention the similarities with the other material mentioned above. It could even be suggested that the differences in composition would have been sufficient to render differences in colour of the freshly struck coins (Plate 95), and that the compositions represent different intrinsic values. Maybe the increased amount of tin in the pellets compensated for the reduction in size and lack of zinc and silver? Perhaps we are just seeing material deposited at the time when large copies gave way to minims in that area?

The division of the compositions into major and minor components clearly demonstrates the existence of more than one batch of alloy being represented in the samples, and that the major components were closely controlled. These facts argue strongly for two distinct and controlled alloy standards being represented in the hoard and that these relate directly to two different size groups and production processes. This is in direct contrast to the accepted view of radiate copies, where it is generally thought that no alloying standards operated; any available metal being melted down for coins (Boon 1988 129).

There is a clear trait in the composition of the radiate copies which should be mentioned, and that is the presence of zinc. Apart from the earlier orichalcum issues (sestertii and dupondii) of the first two and a half centuries AD., zinc is only present as a trace (<0.1%) in 'official' base-metal coins. Indeed, zinc is similarly lacking in both of the later outbreaks of copying discussed here. The radiate copies, however, seem to consistently contain about 1.5% zinc. This trait was confirmed recently by Mike Cowell of the British Museum research laboratories, who analysed two struck copies and three official radiates semi-quantitatively by XRF (Cowell pers comm). What is the significance of the 1.5% zinc, and is the amount purely fortuitous or, as its consistency suggests, a desired component? Certainly other Romano-British metalwork can contain similar amounts of zinc (Bayley 1986.384 for example), but it is the fact that the same amount is maintained over, in the case of Fenny Stratford, what appears to be three melts of metal. The same sort of figure occurs in Mike Cowell's analyses, the Sprotbrough Hoard and the Brauweiler Hoard (Ziegler 1983).

It may also be significant that the high tin pellets contain virtually no zinc. The results of the analyses (XRF) of the copies in the Brauweiler hoard show that copies with recorded zinc values of between 1.5% and 4.00% also tend to have low tin values (<2%) and that copies with higher tin values (>2%) have less zinc (<1%) (Ziegler 1983 76).

The presence of around 1% silver is also consistent with the analysis of the material from the Sprotbrough hoard (Mattingly and Dolby 1982 31), where 1.5% was recorded by electron-probe microanalysis of a polished section. This amount is also consistent with the silver content of the 'official' radiate coins, and may indicate one of two possibilities; the use of official coins in the recipe for barbar ous radiates, or that a serious attempt was being made to produce an alloy of equivalent intrinsic worth.

The analyses of the four copies identified in the Walbottle hoard show very comparable traits in their silver, zinc and tin contents;

	Silver	Zinc	Tin
Gallienus copy	2.33	0.77	4.91
Claudius II copy	0.51	2.52	2.72
Postumus copy	0.71	0.03	2.48
unattributable	0.06	0.56	10.98

TABLE 19. SILVER, ZINC AND TIN CONTENTS OF WALBOTTLE HOARD COPIES.

The Claudius II copy has over 2% zinc as well as over 2% tin, but little silver. The Postumus copy has slightly more silver, no zinc and slightly less tin. The unattributable copy has no silver, little zinc, but a great deal of tin. The Gallienus copy has somewhat more silver and tin than its 'official' prototypes, but also has enough zinc to suggest that it is not over-struck on an earlier (and therefore richer) official radiate. The similarities with Zieglers results are striking, especially considering the inevitable differences caused by Zieglers 'surface only' technique (see chapter 4).

The results of the present study would suggest that it is unlikely that official coins were being melted down and re-coined as copies. There are two main reasons for this. Firstly there can be no logical reason for our local moneyer to melt down official coins only to re-issue coins of not only the same intrinsic value, but also (taking the Fenny Stratford material) of the same weight. One may argue that the reduced size and weight of some copies, such as Sprotbrough or Lydney (Boon 1988 114), would have made such a practice at least economically viable, but this is certainly not the case with the full-weight copies. It also seems improbable when one considers that the likely impetus for these copying epidemics was a shortage of official coins - melting them down is hardly going to improve the situation unless the metal was made to go *considerably* further.

The second reason refers directly to the analytical data. The presence of zinc in the copies alone has been dealt with above, and other elements appear to be present in consistently higher or lower amounts. Lead, iron and tin are all notably higher in the copies, both in the Fenny Stratford material and in other analyses. In other words it is quite apparent that there are too many overall dissimilarities between the alloys used for the official coins (which are predominantly argentiferous coppers) and those used for the copies. This fact is clearly demonstrated by the PCA conducted on all the data sets discussed in chapter 3. Where similarities do exist is primarily in the silver content, which must indicate that this was a consistently added amount and not a fortuitous contaminant.

The principal component analysis of the Walbottle hoard supports this view. The copies are clearly grouped with the issues of the Central empire on the basis of their silver, tin and lead. But are clearly grouped with the Gallic issues by their trace components. This strongly suggests that the copiers were trying to emulate the Central empire issues by manipulating the composition as best they could. However, the characteristic trace element profile gives the origin away as being Gallic.

The final principal component analysis (Chapter 3, section 1.4) suggests that the radiate copies are distinguished from their 'official' prototypes by their zinc, tin, cobalt and nickel levels.

Zinc has already been shown to be diagnostic, as has tin. Cobalt and nickel are less apparent and are trace elements which are likely to relate to the sources of the copper used. Indeed, it is these elements which distinguish between the three 'melts' of alloy discerned within the Fenny Stratford blanks. This is of interest as it serves not only to distinguish between copies and 'official' Central issues, but also between copies and 'official' Gallic issues. Assuming that both Central mints and Gallic mints were using primarily freshly smelted alloying components (lead, copper, tin and silver), then the differences in cobalt and nickel levels represent the differences between the metal used by the 'official' Gallic mints and the metal available to the producers of the copies. This is a small difference, and as demonstrated above, the metal used for both the copies and the 'official' Gallic issues has a very similar trace element profile.

The overall conclusion resulting from this study is that the composition of the copies was controlled to an extent not previously thought. This suggests that despite their, to modern eyes, often excessively crude appearance, their intrinsic worth was maintained within certain parameters. This suggests that the majority of these coins were not the products of overt forgery with the intent to deceive, but the products of semi-official mints. These mints may have been temporary affairs, answering an occasional demand for coinage. This, it has been suggested, was caused by the need to pay (in coin) the large labour gangs employed in the construction of town walls and other large public building projects which are a feature of this period (Davies 1992.221).

5.2.2 The Constantinian Period.

The main contribution of this study to our understanding of this period of copying is in the confirmation of Cathy Kings work on the Woodeaton hoard (1978). As discussed above (chapter 1), King suggests that the copies can only be reliably separated from their prototypes by a compositional analysis. However, this was based on only the one study. The analysis of the sample taken from the Bancroft hoard demonstrates that this is the case in more than one hoard, and that the same trend appears in the site finds from Market Deeping.

The use of AAS for this analysis has also enabled a fuller and more precise compositional picture to be assembled. It was found that the copies were distinguishable from the 'official' issues by more elements then the silver, tin and lead investigated by King (1978). In particular the iron and zinc levels were the most useful. The *lower* iron content of the copies may suggest that a different smelting technology was used in producing the copper. Iron is the element most dependent on the smelting process (Craddock and Meeks 1987.189), and can be used to suggest the technology employed to produce and refine the copper. It has been suggested for earlier periods (Craddock and Meeks 1987) that a low iron content indicates a non-slagging process using rich primary ores, whereas higher iron indicates the use of an iron rich slagging agent or a

sulphide ore which are typically associated with iron minerals (Craddock and Meeks 1987.193). However, this view should be questioned further. The results of the experimental smelting programme based on archaeological evidence from Timna (Israel) demonstrate quite unequivocally that the simple process of refining raw 'black' copper would produce a copper of equally low iron content (Merkel 1990.117). Furthermore, the lack of any archaeological evidence of Roman date for a non-slagging process and any appropriate reconstruction experimentation seriously undermines this model. The available evidence from Roman Timna (Rothenberg 1990) as well as other Roman smelting sites demonstrates the use of iron ore flux with resultant accumulation of massive quantities of slag. The historical documentary evidence (such as Agricola, 1556) also describes the use of iron rich flux for slagging. This process produces raw, 'black' copper with several percent of iron. This would then be fire refined to oxidise the iron (and many other trace metallic impurities). The oxides could then be removed from the surface of the molten copper as a crucible slag. Rich ores were simply never available in the quantities corresponding to the volume of metal produced during the Roman period (Merkel pers. comm.).

The effectiveness of fire refining is demonstrated by Merkel (1990). The lack of evidence for the non-slagging process strongly suggest that the differences in the iron contents are related more to the refining process rather than smelting.

The iron content of copper-alloys from Britain can be summarised as follows;

Period	No. of analyses	Average % Iron
Bronze Age	773	0.05
Iron Age	56	0.18
Romano-British	129	0.27

TABLE 20. AVERAGE IRON CONTENTS OF COPPER-ALLOYS BY PERIOD (AFTER CRADDOCK AND MEEKS. 1987).

These figures suggest that the refining processes in the earlier periods were applied rather more rigorously and effectively than in the Roman period. Certainly the Romans were aware that refining produced a better, more ductile and malleable metal:

> "Bar copper also is produced in other mines, and likewise fused copper. The difference between them is that the latter can only be fused, as it breaks under the hammer, whereas bar copper, otherwise called ductile copper, is malleable, which is the case with all Cyprus copper. But also in the other mines, this difference of bar copper from fused copper is produced by treatment; for all copper after impurities have been rather carefully removed by fire and melted out of it becomes bar copper.....At Capua it is smelted in a fire of wood, not of charcoal, and then poured into cold water and cleaned in a sieve made of oak....this process of smelting is repeated several times...." (Pliny Book 34. 94-95)

However, it would seem that the more 'traditional' technologies of the native Britons also utilised a rigorous refining process. Furthermore, from the forgoing analyses, the native Britons appear to have used this technology in areas of copper production that the Roman mint authorities did not.

A small amount of iron is lost on each remelting (Merkel 1990), but low levels of iron, below ≅200 ppm, are readily achieved by fire refining. This may well reflect a smaller scale operation where the time and fuel spent on repeated refining was not regarded as wasteful and un-necessary. It may also reflect the values of a more 'traditional' society.

The average iron values for the Bancroft copies is 0.05% (0.05 sd), whereas the average for the 'official' issues is 0.51% (0.3 sd). This would suggest the use of a more refined copper. However, the majority of analyses of Romano-British domestic copper-alloy artefacts do have markedly higher iron contents (Tylecote 1986.37). This suggests that the copies were produced from specially refined metal. This metal may be smelted and especially refined for the production of the 'copies', or it may be especially refined scrap. The refining process investigated by Merkel also suggests the possibility of ancient recovery of some alloying components such as tin and arsenic from the crucible slag (Merkel 1990.118).

The higher zinc content would support the view that the metal from which the copies were made was derived from the same general catchment pool as the domestic metalwork. However, the high loading given the zinc values in the PCA is largely down to one coin with a zinc content of 0.96%. This significantly reduces the importance of the zinc, although the fact of this one coin with such a high zinc content suggests that at least some of the copies were produced from an alloy similar to that employed in making domestic artefacts.

The study of the coins from the Tingrith hoard supports the view that a previously unacknowledged number of these earlier coins are likely to be the products of un-/semi-official mints. However, the compositional differences between these 'copies' and their prototypes can still be ambiguous and unclear. Furthermore, it appears that the composition of these 'copies' is similar enough to that of the 'official' issues of the London mint to suggest a common metal supply pool during this period. This may well suggest that significantly less well-refined scrap metal was added to the alloy than in the previous period.

The analytical results show that the 'official' issues were clearly attempting to adhere to a particular compositional 'ideal' or recipe, but on a grand scale. However, local traditions and circumstances enable small differences to be picked out allowing a clear grouping according to mint to be distinguished. Furthermore, there is a significant correlation between the lead and tin

contents of the 'official' coins strongly suggesting that the lead and tin were added together as a pre-mixed alloy. This view has already been suggested for the post-reform folles of Diocletian (Cope 1968.138) and its continuation here further supports the view of a centrally controlled mint system.

5.2.3 The 'Fel. Temp.' period.

This is the period which has previously seen the least archaeometallurgical interest. The work presented in this thesis is of particular interest as it comes from north of Hadrians wall. The main discovery is the tying in of significant compositional difference with the two coins which appear to be of cruder style. This is important, especially considering that the copies identified here are not reported as copies in the current literature (Brickstock 1987.312). Both copies have lower silver contents than the 'official' issues, but still have only about 0.5% silver. What is particularly interesting is the fact that, like the Bancroft copies, these coins have significantly lower iron contents (0.01% and 0.02% respectively). This must again reflect the level of refining, whether of freshly smelted metal or the further refining of scrap. However, the presence of silver in the alloy at levels which indicate deliberate alloying[15] , suggests that these copies were *not* produced from melted down and de-silvered official coins.

Within the 'official' coins represented the previously published analytical data has been questioned, with particular reference to Ravetz' (1963) NAA studies. The main result of the dissimilarity is to refute the suggestion that the AD 348 reform saw the introduction of coins with a considerably enhanced silver content. The results here show that the new coins, whilst being larger, contained about the same amount of silver as the pre-reform coins (≅1% - Ravetz 1963). Certainly, the silver content of the post-reform AE2 (emperor on galley type) is no where near the 2.5% usually quoted in the literature (Burnett 1987.133; Depeyrot 1982. ; Haley 1989.106).

The other point of interest is in the comparison of coins struck for the 'legitimate' ruler, Constantius II and those struck for the usurper, Magnentius. Both rulers issued coins at Trier, but not at the same time, Magnentius' ill-fated revolt issuing coins only between AD 350 and AD353 (Carson et.al. 1978). The silver contents are maintained at a broadly similar level regardless of ruler, as indeed are the majority of components, indicating that the mint was operating in the same fashion throughout this period. A plot of the iron and nickel values, however, produces an interesting result (fig.70).

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15 The removal of silver by a process of liquation and cupellation would result in silver levels of about 0.0025% (Tylecote 1986.69).

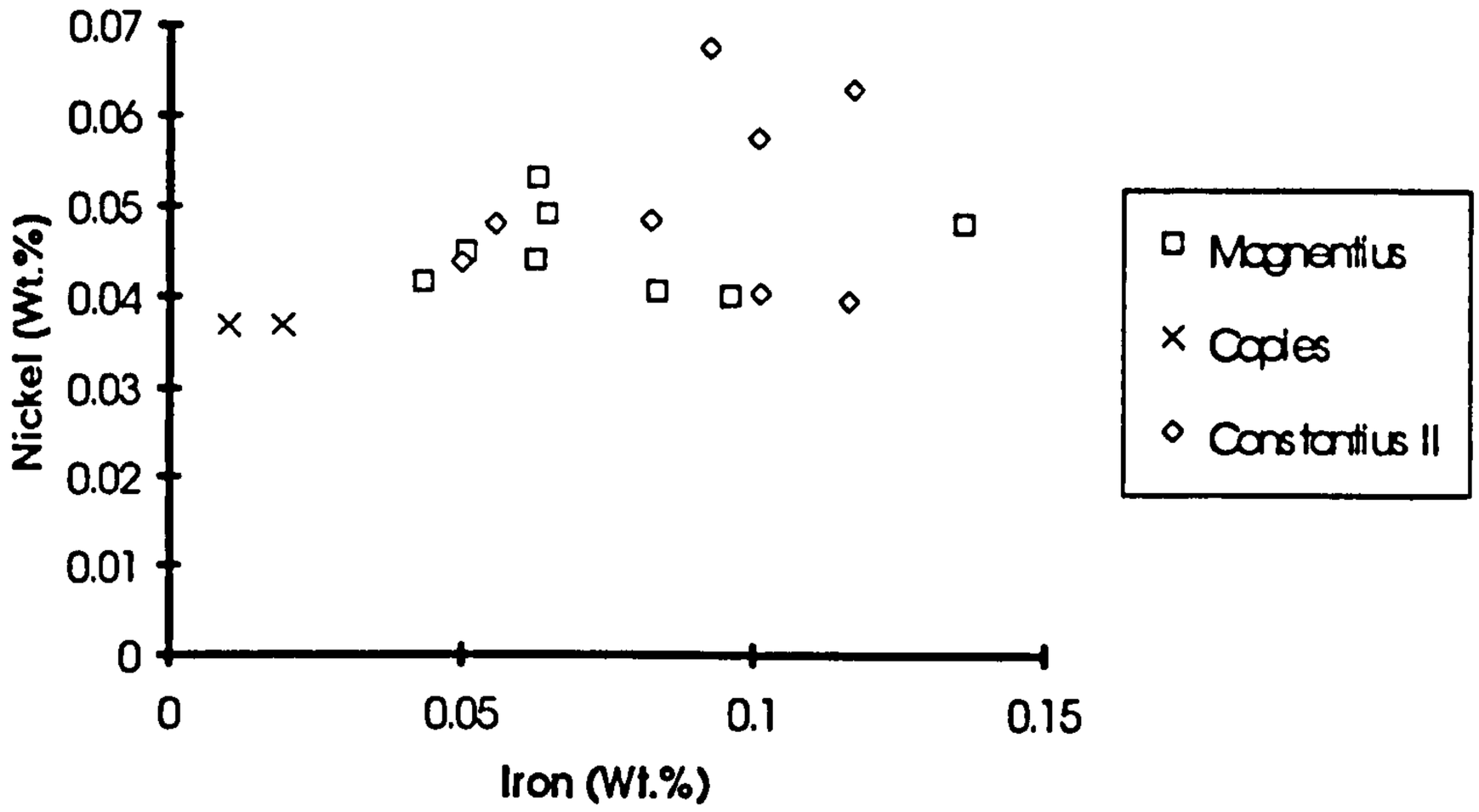


FIG 70. PLOT OF IRON AND NICKEL VALUES FOR STONEYKIRK.

There is a tendency for the coins issued in the name of Magnentius to have a lower iron content than those issued in the name of Constantius II. This is not as marked as the iron content of the copies, but sufficient to suggest that the production and refining of copper differed slightly under Magnentius.

The accepted view of the Fel. Temp. copies has been summed up by Brickstock (1987),

> "...the galley type of 348-50 was widely counterfeited after the illegal removal of the valuable silver from the regular alloy, as were the early types of Magnentius which followed it. The main wave of copying, however, belongs to the years 354-c.364, initially a response to the demonetisation of [all] earlier billon coinage by edict on the 8th March 354, and continued when later coin types failed to circulate widely in Britain.....copying was on a rapidly decreasing module with declining faithfulness to the original AE2....Overstriking and the production of large module copies belongs to the earlier years c.354-357/8. Small module copies were almost certainly produced beyond that date...." (Brickstock 1987.118)

The copies from the Stoneykirk hoard would belong to the earlier period, being copies of Magnentius' FELICITAS REIPVBLICE type (issued from Jan. 350 to spring 351). The analysis, however suggests that these were not produced from de-silvered 'official' issues, or overstruck on de-monetised pre-reform coins. The fact that the silver contents are consistent with the pre-reform coins (see chapter 3 for details) supports the overstriking hypothesis. It is the low iron and nickel values which mark these copies out as fundamentally different. Furthermore, comparison with the iron and nickel values of the 'official' Bancroft villa hoard coins would clearly reject any suggestion that the pre-reform coins had lower iron contents. It therefore seems hard to escape from the conclusion that some, at least, of the early copies were produced from a specially prepared alloy which contained about 0.5% silver. It is the later, smaller copies of the North Leigh and Lydney types which support the view of de-silvered metal from melted down de-monetised issues being re-struck as copies of the fallen horseman types. Certainly Brickstocks

suggestion of a two phase period of copying is supported by the analysis, although more work needs to be done to establish the nature of the initial phase.

5.2.4 General considerations

Each period of copying was a different response to a broadly similar phenomenon, the lack of low value coins to maintain a rapidly monetising economy. The late third century responded with copies which generally bore very little resemblance to their prototypes, yet which appear to conform to very particular requirements of composition, often mirroring the composition of the 'official' coins quite closely. These requirements could relate to the control of the intrinsic value of the coins.

The response during the 330's saw the production of very carefully produced copies which only differ significantly in their composition. These copies contain very little silver and a lot of lead. Here, the visual aspect of the coins was important, not what was in them.

The FTR copies appear to start as reasonably accurate copies, either over-striking de-monetised issues without removing the silver beforehand, or producing an alloy with a silver content mirroring that of the de-monetised coins. Later, copies were produced from de-silvered metal in a similar fashion to the previous period.

We can boil this down to two types of response. Firstly, the production of coins which are obviously the products of non-official mints, but which have a controlled intrinsic value involving the addition of small amounts of silver, tin and orichalcum. Secondly, the production of fairly carefully produced copies in metal which may well be the product of de-silvering 'official' issues. The final point is that both classes of copy appear to have circulated alongside their 'official' prototypes (King 1981.46).

In conclusion, although to our modern perceptions, the radiate copies and the FTR copies bear little resemblance to the 'official' coins, they were perceived by their users to be of equal value (see Boon 1988 for a discussion of this). Furthermore, the analysis suggests that, despite appearances, the alloy for these copies was being produced to a regulated standard. This standard seems to be one related more to a particular intrinsic value than a particular composition, zinc, silver and tin apparently being interchangeable in the radiate copies. This must suggest a very different attitude to what constitutes 'authentic' legal tender. Perhaps the mere suggestion of the emperors 'imago' on a coin was sufficient for it to be perceived as 'authentic'. The concept of 'authentic' can be seen as "a cultural construct of the modern Western world" (Handler 1986.2). Our concept of what constitutes 'authenticity' is closely tied to our notions of individualism. This is a modern view. The ancient and medieval world was seen as a whole, encompassed and

ordained by God, or gods. Each person was merely a part of that whole, subsumed within the cosmos. This same view can be seen within more traditional societies today, where the idea of 'authentic' is very different to what we would consider as 'the real thing'. This difference in perception is much of the reason why it is hard for us to appreciate how the copies and 'official' coins could be viewed as equivalent. If this anthropological link seems tenuous, then the reader is referred to Handler (1986) for a fuller discussion. We must not forget that we are dealing with a more traditional society than today's, to which coinage itself was a relatively new idea. Many of the societies more ancient and deeply rooted traditions would still play a significant role in the use, and more importantly, production of coinage.

This view is supported by the way in which the Fenny Stratford blanks were produced (see chapter 3). The metallographic examination of the 'pre-blanks' indicates that they were individually cast in open moulds. This method would be consistent with the evidence from Iron age sites such as Prae Wood (St.Albans) and Old Sleaford (Lincs.) (Tylecote 1986.114) where clay moulds have been found. This method of production is seen by Bayley (1992.180) as a 'diagnostic type fossil' for the Late pre-Roman Iron age (LPRIA), the occurence of moulds in later contexts being regarded as residual. The occurence of material which was clearly produced by this LPRIA 'type fossil', in what must be seen as a late third century context, would strongly suggest the continuation of pre-Roman techniques and production traditions well after the conquest. If this tradition continued, then one could argue for the continuation of other traditional LPRIA metalworking techniques and attitudes as well.

The use of minor additions of particular metals to alloys destined for particular functions is reported in Tibetan and Indian bronzes (Lo Bue 1981). For example, the use of *pancha loha* - or five-metalled alloy - is reported to be preferred for the making of images. This metal is an alloy of gold, silver, copper, lead and tin, each component representing one of the basic elements - thus the body of the image can be said to be composed of the five elements themselves (Nagaswamy 1988. 146). These components serve no metallurgical purpose and were added because tradition and the texts said that this was the way this particular alloy should be prepared. Furthermore, the actual alloys are often at variance with the texts prescribing the composition of the alloys, a very loose interpretation being seemingly appropriate (Lo Bue 1981.33). A similar model can be proposed for the production of semi-/ un-official coins in Roman-Britain. The presence of amounts of silver, zinc, lead and tin need not have a metallurgical or even the economic role suggested above, they may merely represent an interpretation of what a coinage alloy *should* consist of. We may be seeing the copying of an *idea* of coinage rather that an attempt to reproduce a specific reality. Certainly, the fact that the copies appeared to circulate alongside and were treated as equal to the 'official' coins suggests that it was the *idea* that was all important.

5.3 Discussion of results from the archaeometallurgical standpoint.

The accepted techniques for 'non-destructively' analysing complex copper-alloy coins are not sufficiently rigorous to allow for accurate compositional profiles to be suggested. The mechanical removal of 15 μm or so of surface metal advocated in the literature (Carter 1964 etc.) is rarely sufficient to remove the entire zone of metal which has been altered by segregation during manufacture and/or post-depositional processes (surface enrichment/depletion). The several studies conducted by Carter (1964, 1967, 1983, 1984, 1986) have all used 'pure' copper or simple binary alloy (orichalcum) coins for which such preparation and analytical proce dures can be adequate. Furthermore, if the numismatic/archaeological questions being addressed by the analysis only require a limited degree of accuracy (to within say 1%) then a 'non-destructive' analysis may well be sufficient. However, if statistical methods (such as discriminant analysis - see Carter 1993) are to be applied, then greater accuracy is required in order to establish that the structure found is attributable to the numismatic and/or historical reasons suggested.

The degree of corrosion affecting a coin can also severely alter the perceived composition *regardless* of the analytical technique employed. The degree of alteration varies from element to element, and is also dependent on the severity of the corrosion. However, the factors governing these effects are too complex to allow any form of quantification. Iron has been shown to be the element most strongly related to the degree of corrosion, but also one of importance in the archaeological interpretation of the material. Consequently it is of paramount importance to understand to which phenomena a perceived variation in iron content is due. The low levels at which iron occurs in most copper-alloy coins makes both precision and sensitivity of prime importance. Furthermore, it has also been shown that the concentration of iron can be substantially increased towards the surface of a coin due to the corrosion processes. This is obviously similar in effect to 'surface enrichment/depletion' experienced by other elements, but is the product of iron permeating in from the surrounding ground water and being re-deposited within the surface copper matrix. In the same way it is important that any analysis avoids this effect. The lead content has also been shown to be strongly related to the severity of corrosion, and also the regionality of the phenomona encountered. The high levels of lead in many ancient copper-alloys means that its effects have wide reaching repercussions. Its insolubility in the copper matrix coupled with its electronegativity give it a crucial role in the corrosion processes and are phenomena already documented in the literature (Condamin and Picon 1972). Furthermore, the greater solubility of a number of elements in lead rather than in copper (notably silver, arsenic and tin) means that the presence of high levels of lead can significantly affect the levels and distribution of other elements as well, and consequently the levels of accuracy achieved in an analysis which may be sensitive to such factors.

It has also been suggested that the high levels of lead may have been maintained in order to facilitate the creation of a 'white metal' coating on the surface of the freshly struck coins. Cope (1972a.276) refers to a lead-sheen on some later fourth century coins and the work of Bernard et al. (1980) suggests the use of a tin/silver-sweat on Celtic coins. This effect appears to have been produced by the squeezing of a liquid tin-rich phase to the surface of the coin blank during striking. The EPMA work presented here suggests that a similar phenomena may well have been exploited in the production of 'silvered' copper-alloy coins from the later third-century.

Much, obviously, depends upon the quality of the data required, and upon the archaeological questions being asked of it. This thesis has demonstrated that useful insights into the problems associated with one particular area of Romano-British numismatics and archaeology can be gained by the investigation of elemental 'profiles'. The use of standard multivariate statistical techniques together with basic descriptive methods has been used to look for subtle levels of structure within data sets derived using a careful sampling proce dure. Because of the subtleties of the data, it has been necessary to demonstrate that the structure picked up by the techniques employed are attributable to the inferred history of the artefact and not the result of corrosion processes or cleaning.

The combination of EPMA, AAS and metallography shows that the effects of corrosion and segregation in the complex and highly leaded copper-alloys used in later Roman coinage cannot be adequately circumvented by the accepted sampling and analytical proce dures. What is meant by 'adequately' here, is a proceedure which will allow the sufficient precision of analysis required to establish the type of compositional 'profile' explored in this thesis. It is certainly possible to obtain good semi-quantitative analyses by this method which can enable very general statements to be made. However, in order to discuss alloy standards in terms of 'scupulae per libra', differences in production technique between mints, and the differences in technology and the metal supply areas, a greater degree of rigour is required. Furthermore, a clearly defined sampling strategy needs to be established relative to each formulated archaeological question. The results of this study clearly show that it is important to compare material which has been exposed to similar environmental conditions. It is not good enough simply to rely on,

> "....the generosity of a number of numismatists and museum authorities...." (Cope 1968.118)

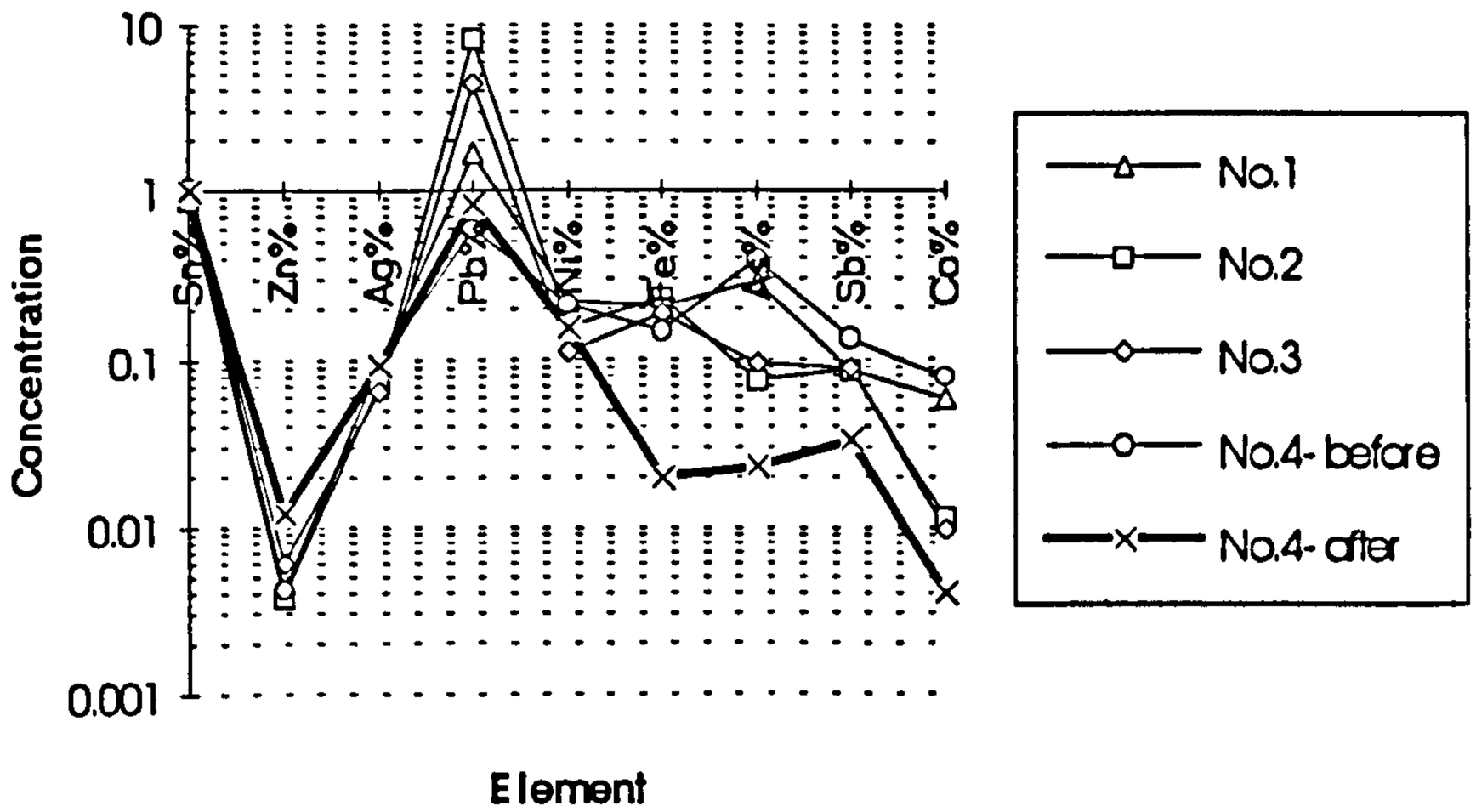
The comparison of results between Richborough and Tingrith, and between Market Deeping site finds and the hoard material clearly demonstrates this point. The use of representative samples has also been discussed and the importance demonstrated. The number of analyses conducted on a particular class of coin is clearly crucial to the robustness of any inferences made from the resultant data.

Future work will inevitably improve and refine the findings presented here as questions and proce dures are refined. The suggestions made concerning the periods of copying need to be explored more fully, looking at a larger and more varied set of well-attributed samples. However, the importance and validity of the approach to archaeology in general and numismatics in particular have been assessed. Surely the value of the data obtained, and its inferences, far outweigh any considerations of market value in the antiquities trade. Furthermore, the degree of damage inflicted by the micro-sampling technique used here is no worse than that inflicted by the abrasion advocated as non-destructive.

APPENDICES

Appendix 1.

Four numismatically identical coins were each sampled by the usual drilling method and the drillings were then analysed by AAS. The coins were copper-alloy issues of Theodosius II with the CONCORDIA AVGG reverse type (LRBC 2676). The fourth coin analysed was then chemically stripped using 10% formic acid. The coin was soaked in the solution for ten hours, soaked in de-ionised water for a further ten hours, rinsed in de-ionised water and air dried. The results were then compared in the plot shown below.



The four coins analysed un-stripped all have very similar compositions as would be expected. It is only the lead concentration which varies significantly, and this is again as expected given the insolubility of lead. The analysis of coin number four after 'cleaning', however, does show significant differences in the concentration of certain constituents. Four of the trace components are significantly reduced in concentration (iron, arsenic, antimony and cobalt). This strongly suggests that this method of cleaning can significantly alter the composition, even at the trace element level.

The logarithmic plot was used in order to easily compare rather different concentration levels. The real values are tabulated below.

	Sn%	Zn%	Ag%	Pb%	Ni%	Fe%	As%	Sb%	Co%
No.1	0.983	0.004	0.095	1.654	0.223	0.204	0.286	0.085	0.058
No.2	0.863	0.004	0.073	8.213	0.158	0.231	0.075	0.086	0.011
No.3	1.077	0.006	0.065	4.366	0.111	0.187	0.096	0.089	0.010
No.4- before	1.050	0.004	0.094	0.594	0.210	0.148	0.387	0.131	0.077
No.4- after	0.986	0.012	0.093	0.833	0.153	0.020	0.023	0.033	0.004

Appendix 2. All Data.

No.	Cu%	Sn%	Zn%	Ag%	Pb%	Au%	Ni%	Fe%	As%	Sb%	Co%	Cr%	Total%
5	89.8	4.07	1.33	0.96	4.71	0.016	0.043	2.307	0.037	0.117	0.009	0.002	103.4
6	86.0	6.14	1.27	0.97	7.72	0.019	0.041	0.290	0.058	0.158	0.012	0.003	102.7
7	99.2	3.83	1.44	1.01	6.16	0.026	0.050	0.894	0.050	0.129	0.006	0.004	112.8
8	88.6	4.77	1.35	0.93	5.24	0.026	0.041	0.859	0.036	0.117	0.010	0.005	102.0
9	85.9	4.74	1.41	1.30	5.45	0.024	0.050	0.842	0.039	0.122	0.011	0.004	99.9
10	88.5	4.75	1.43	0.87	5.63	0.028	0.046	0.759	0.063	0.129	0.011	0.003	102.2
11	87.8	4.90	1.42	1.05	5.64	0.023	0.021	0.776	0.037	0.115	0.010	0.002	101.8
12	91.1	4.02	1.32	0.89	5.51	0.027	0.019	0.848	0.046	0.103	0.010	0.003	103.9
13	86.2	3.87	1.44	0.92	5.72	0.026	0.020	0.508	0.050	0.122	0.014	0.005	98.9
14	90.3	5.07	1.31	1.17	5.56	0.025	0.021	0.889	0.035	0.119	0.014	0.003	104.5
15	91.2	3.72	1.37	0.95	5.97	0.027	0.020	0.498	0.023	0.131	0.013	0.006	103.9
16	84.1	4.64	1.36	1.05	5.38	0.032	0.021	0.757	0.012	0.125	0.005	0.005	97.5
17	85.4	4.99	1.44	0.93	6.34	0.039	0.021	0.454	0.025	0.120	0.009	0.005	99.7
18	87.9	4.59	1.41	0.92	5.51	0.038	0.025	0.758	0.038	0.099	0.009	0.005	101.3
19	84.3	6.47	1.60	1.17	6.33	0.040	0.032	0.512	0.039	0.108	0.010	0.006	100.6
20	91.5	4.50	1.35	0.68	5.35	0.035	0.012	0.906	0.035	0.120	0.011	0.007	104.6
21	87.4	3.59	1.37	0.47	5.46	0.029	0.012	0.713	0.049	0.123	0.013	0.009	99.3
22	86.1	3.56	1.40	0.87	5.30	0.021	0.013	0.846	0.026	0.111	0.013	0.009	98.3
23	90.7	4.71	1.28	1.04	5.69	0.016	0.010	0.743	0.011	0.117	0.011	0.007	104.3
24	83.2	5.99	1.23	0.73	7.51	0.024	0.007	0.272	0.036	0.151	0.004	0.007	99.2
25	85.2	5.13	1.44	0.84	4.86	0.020	0.010	0.501	0.038	0.117	0.124	0.008	98.3
26	89.4	4.86	1.31	1.00	5.64	0.023	0.024	0.756	0.011	0.118	0.009	0.009	103.1
27	82.6	6.44	1.25	0.87	8.06	0.026	0.025	0.269	0.013	0.140	0.009	0.000	99.7
28	85.3	4.89	1.45	1.00	5.34	0.023	0.024	0.655	0.000	0.124	0.010	0.000	98.8
29	84.8	4.57	1.40	0.73	5.29	0.030	0.026	0.808	0.026	0.114	0.014	0.000	97.8
30	86.9	4.82	1.45	0.84	4.95	0.024	0.028	0.750	0.000	0.121	0.006	0.000	99.9
31	87.4	4.42	1.46	1.00	5.08	0.018	0.000	0.758	0.000	0.115	0.242	0.008	100.5
32	82.9	3.67	1.36	0.52	5.22	0.006	0.000	0.821	0.000	0.114	0.011	0.001	94.6
33	88.1	4.47	1.45	1.00	5.18	0.006	0.000	0.793	0.063	0.107	0.009	0.000	101.1
34	86.2	3.53	1.46	0.61	5.32	0.010	0.000	0.742	0.051	0.117	0.011	0.003	98.0
35	85.0	12.57	0.10	0.09	7.21	0.010	0.000	0.655	0.000	0.117	0.017	0.002	105.8
38	80.6	13.62	0.08	0.07	7.87	0.005	0.035	0.781	0.033	0.131	0.004	0.004	103.2
39	80.2	13.22	0.10	0.08	7.40	0.010	0.039	0.470	0.025	0.109	0.005	0.005	101.6
40	84.0	13.99	0.12	0.08	7.35	0.007	0.036	0.479	0.023	0.097	0.007	0.002	106.2
41	77.7	13.89	0.13	0.07	8.34	0.000	0.033	0.589	0.000	0.108	0.009	0.005	100.9
42	78.1	14.40	0.14	0.07	8.28	0.001	0.032	0.612	0.000	0.113	0.010	0.002	101.7
43	78.2	12.81	0.13	0.07	8.06	0.004	0.033	0.572	0.012	0.103	0.011	0.005	100.0
44	78.3	13.16	0.26	0.07	6.93	0.007	0.037	0.940	0.011	0.121	0.009	0.006	99.9
45	76.3	13.49	0.07	0.07	7.85	0.006	0.036	0.854	0.000	0.111	0.012	0.006	98.8
46	79.8	13.15	0.11	0.08	7.44	0.005	0.030	0.418	0.024	0.117	0.013	0.006	101.2
47	80.5	12.38	0.10	0.08	7.28	0.004	0.030	0.463	0.000	0.113	0.013	0.009	101.0
48	79.7	13.64	0.08	0.11	7.97	0.004	0.035	0.782	0.047	0.131	0.012	0.002	102.5
49	81.6	12.45	0.12	0.08	7.32	0.006	0.030	0.424	0.000	0.101	0.004	0.003	102.1

FENNY STRATFORD HOARD ANALYTICAL DATA

No.	Emperor	RIC/Elmer	Mint	Ag%	Zn%	Sn%	Sb%	Cr%	Co%	Au%	Ni%	Fe%	Pb%	As%	Cu%	Total
1	Valerian	RIC71	Rome	30.29	0.12	1.18	0.09	0.11	0.05	0.13	0.08	0.01	0.96	0.36	67.31	100.7
2	Gallienus-joint	RIC175	Rome	4.32	0.13	2.5	0.15	0.11	0.11	0.16	0.07	0.14	2.57	0.02	88.73	99
3	Gallienus-joint	RIC392	Mlan	2.04	0.095	5.96	0.2	0.51	0.43	0.36	0.15	0.1	1.58	1.66	88.46	101.5
4	Gallienus-sole	RIC572	Sisda	1.26	0.031	6.09	0.113	0.05	0.035	0.11	0.051	0.042	3.12	0.08	88.6	99.6
5	Gallienus-sole	RIC575	Sisda	0.85	0.04	1.17	0.057	0.05	0.029	0.04	0.037	0.039	1.36	0.15	93.89	97.7
6	Gallienus-sole	RIC499	Mlan	1.56	0.037	1.15	0.086	0.05	0.069	0.04	0.04	0.031	1.29	0.47	87.15	92
7	Gallienus-sole	RIC499	Mlan	1.58	0.17	1.09	0.073	0.05	0.026	0.05	0.05	0.073	1.9	0.02	98.1	103.2
8	Gallienus-sole	RIC534	Mlan	7.67	0.11	1.19	0.08	0.05	0.293	0.17	0.085	0.112	1.3	0.02	88.25	99.3
9	Gallienus-sole	RIC157	Rome	1.36	0.113	7.96	0.57	0.46	0.11	0.15	0.05	0.01	1.13	0.62	82.24	94.8
10	Gallienus-sole	RIC157	Rome	1.1	0.092	5.94	0.093	0.05	0.071	0.03	0.048	0.057	5.79	0.02	88.98	102.3
11	Gallienus-sole	RIC157	Rome	1.74	0.127	5.66	0.151	0.05	0.111	0.05	0.059	0.061	3.68	0.92	92.41	105
12	Gallienus-sole	RIC177	Rome	1.62	0.082	7.67	0.042	0.11	0.085	0.05	0.069	0.098	10.64	0.2	82.2	102.9
13	Gallienus-sole	RIC193var	Rome	2.69	0.06	7.16	0.186	0.13	0.074	0.12	0.066	0.073	3.18	0.11	71.43	85.3
14	Gallienus-sole	RIC236	Rome	1.49	0.14	6.55	0.269	0.19	0.077	0.06	0.062	0.045	2.42	0.21	94.19	105.7
15	Gallienus-sole	RIC236	Rome	1.67	0.05	6.12	0.121	0.29	0.061	0.05	0.038	0.096	3.35	0.02	90.91	102.8
16	Gallienus-sole	RIC280	Rome	0.72	0.08	6.25	0.58	0.26	0.08	0.04	0.06	0.02	3.57	0.2	92.59	104.5
17	Gallienus-sole	RIC287var	Rome	1.81	0.138	6.03	0.156	0.3	0.066	0.05	0.041	0.045	5.07	0.05	92.14	105.9
18	Gallienus-sole	RIC249/494	Rome/Mlan	1.41	0.071	1.56	0.153	0.05	0.058	0.05	0.043	0.022	4.51	0.39	89.29	97.6
19	Salonina-joint	RIC29	Rome	2.16	0.059	4.26	0.244	0.05	0.078	0.12	0.041	0.065	1.13	0.02	95	103.2
20	Salonina-joint	RIC29	Rome	1.74	0.027	1.03	0.198	0.05	0.091	0.07	0.049	0.036	2.44	0.02	97.55	103.3
21	Salonina-sole	RIC5	Rome	1.56	0.076	5.17	0.33	0.05	0.084	0.03	0.049	0.041	3.63	0.21	87.5	98.7
22	Salonina-sole	RIC5	Rome	1.55	0.074	6.01	0.223	0.06	0.079	0.04	0.064	0.048	2.67	0.02	93.51	104.3
23	Claudius II	RIC191	Sisda	1.27	0.061	2.61	0.164	0.08	0.077	0.02	0.047	0.046	3.02	0.02	92.97	100.4
24	Claudius II	RIC149	Mlan	1.88	0.033	4.38	0.23	0.12	0.139	0.02	0.068	0.068	3.66	0.02	95.09	105.7
25	Claudius II	RIC157	Mlan	1.27	0.057	5.14	0.08	0.05	0.095	0.04	0.077	0.095	3.42	0.1	88.79	99.2
26	Claudius II	RIC46	Rome	1.49	0.114	7.35	0.187	0.06	0.079	0.01	0.06	0.062	8.45	0.02	85.26	103.1
27	Claudius II	RIC62	Rome	1.35	0.285	6.15	0.175	0.04	0.081	0.02	0.043	0.072	9.93	0.02	87.23	105.4
28	Claudius II	RIC91	Rome	1.28	0.072	5.75	0.154	0.07	0.142	0.02	0.047	0.047	12.82	0.02	80.97	101.4
29	Claudius II	RIC104	Rome	0.85	0.071	6.98	0.093	0.06	0.042	0.02	0.048	0.076	7.89	0.02	79.04	95.2
30	Claudius II	RIC104	Rome	1.83	0.121	7.67	0.709	0.05	0.214	0.03	0.073	0.184	7.15	0.02	84.16	102.2
31	Claudius II	RIC104	Rome	1.3	0.097	5.61	0.1	0.05	0.075	0.03	0.051	0.054	7.19	0.15	84.74	99.5
32	Claudius II	RIC104	Rome	0.73	0.088	6.61	0.096	0.05	0.067	0.01	0.061	0.081	8.43	0.28	81.03	97.5
33	Claudius II	RIC109	Rome	1.11	0.107	5.99	0.102	0.05	0.096	0.02	0.07	0.068	9.86	0.02	75.71	93.2
34	Claudius II	RIC109	Rome	1.21	0.056	6.6	0.105	0.08	0.081	0.02	0.086	0.078	10.72	0.02	77.4	96.5
35	Claudius II	RIC261	Mlan com.	0.94	0.195	5.21	0.123	0.04	0.085	0.02	0.053	0.068	6.24	0.02	83.98	97
36	Claudius II	RIC261	Mlan com.	0.08	0.045	5.73	0.108	0.04	0.049	0.01	0.05	0.026	15.7	0.02	75.77	97.6
37	Claudius II	RIC266	? comm.	0.86	0.153	5.78	0.118	0.06	0.068	0.01	0.063	0.127	12.98	0.02	75.71	95.9
38	Claudius II	RIC266	? comm.	1.05	0.147	4.89	0.129	0.09	0.05	0.02	0.087	0.085	6.63	0.02	82.71	95.9
39	Quintillus	RIC26	Rome	0.8	0.06	7.01	0.11	0.11	0.07	0.02	0.05	0.03	8.34	0.02	82.49	99.1
40	Quintillus	RIC33	Rome	0.74	0.1	5.91	0.02	0.07	0.07	0.01	0.04	0.03	6.49	0.02	83.33	96.8
41	Aurelian	RIC38	Rome	0.56	0.15	6.02	0.05	0.05	0.02	0.02	0.03	0.09	10.99	0.02	79.41	97.4
42	Postumus	E299		0.57	0.12	1.79	0.04	0.09	0.05	0.03	0.03	0.13	0.78	0.02	95.25	98.9
43	Postumus	E299		8.26	0.03	0.23	0.09	0.11	0.06	0.09	0.05	0.01	0.91	0.02	89.64	99.5
44	Postumus	E335		22.22	0.11	0.79	0.21	0.06	0.06	0.12	0.06	0.03	1.41	0.02	77.73	102.8
45	Postumus	E335		16.47	0.06	0.01	0.14	0.11	0.08	0.15	0.04	0.04	1.27	0.02	83.65	102
46	Postumus	E566		0.83	0.033	0.16	0.153	0.05	0.014	0.01	0.025	0.037	1.74	0.11	97.07	100.2
47	Postumus	E566		3.95	0.031	0.21	0.13	0.05	0.02	0.03	0.028	0.019	1.4	0.12	99.39	105.4
48	Postumus	E568		1.92	0.021	0.08	0.123	0.05	0.011	0.02	0.023	0.012	0.87	0.07	76.7	79.9
49	Postumus	E568		3.27	0.057	0.18	0.099	0.05	0.01	0.02	0.032	0.01	0.84	0.1	80.41	85.1
50	Victorinus	E741		1.09	0.093	0.30	0.192	0.050	0.006	0.01	0.044	0.062	2.64	0.12	95.51	100.1
51	Victorinus	E741		0.64	0.106	1.66	0.119	0.050	0.005	0.01	0.040	0.163	2.29	0.11	98.26	103.4
52	Victorinus	E743		0.82	0.241	0.19	0.165	0.050	0.007	0.01	0.038	0.164	1.74	0.14	94.60	98.2
53	Victorinus	E743		0.81	0.045	0.02	0.216	0.050	0.006	0.01	0.048	0.010	2.59	0.12	96.27	100.2
54	Victorinus	E699		0.66	0.042	0.17	0.165	0.050	0.006	0.01	0.052	0.048	2.00	0.12	99.00	102.3
55	Victorinus	E699		0.94	0.081	0.12	0.183	0.050	0.005	0.01	0.010	0.099	1.90	0.10	96.36	99.9
56	Victorinus	E732		0.76	0.030	0.10	0.162	0.050	0.010	0.01	0.013	0.154	1.07	0.08	95.73	98.2
57	Victorinus	E732		0.75	0.059	0.24	0.130	0.050	0.010	0.01	0.028	4.511	1.06	0.10	95.45	102.4
58	Victorinus	E682		0.48	0.059	0.32	0.134	0.050	0.005	0.01	0.026	0.103	1.57	0.11	97.13	100.0
59	Victorinus	E682		0.34	0.016	0.09	0.120	0.050	0.009	0.01	0.022	0.020	1.83	0.09	94.83	97.4
60	Victorinus	E682var		1.52	0.061	0.32	0.118	0.050	0.013	0.02	0.020	0.007	2.30	0.12	94.55	99.1
61	Victorinus	E682var		2.28	0.067	0.20	0.108	0.050	0.013	0.02	0.023	0.025	1.70	0.13	97.82	102.4
62	Victorinus	E683		1.60	0.028	0.21	0.147	0.050	0.014	0.02	0.032	0.065	1.60	0.12	99.07	103.0
63	Victorinus	E683		2.16	0.068	0.17	0.127	0.050	0.007	0.01	0.032	0.157	1.71	0.08	97.21	101.8
64	Victorinus	E683var		1.81	0.038	0.26	0.115	0.050	0.019	0.02	0.045	0.016	2.18	0.13	97.89	102.6
65	Victorinus	E683var		0.86	0.027	0.24	0.140	0.050	0.019	0.03	0.011	0.020	1.63	0.12	97.21	100.4
66	Tetricus I	E774		0.70	0.038	0.24	0.118	0.050	0.006	0.01	0.012	0.120	1.95	0.12	95.86	99.2
67	Tetricus I	E774		0.66	0.058	0.07	0.145	0.050	0.006	0.01	0.011	0.086	1.21	0.11	96.65	99.1
68	Tetricus I	E764		0.72	0.213	0.15	0.139	0.050	0.005	0.01	0.010	0.042	2.08	0.10	94.17	97.7
69	Tetricus I	E764		0.59	0.024	0.32	0.066	0.050	0.005	0.01	0.011	0.024	2.35	0.11	98.06	101.6

WALBOTTLE HOARD ANALYTICAL DATA

No.	Emperor	RIC/Elmer	Mint	Ag%	Zn%	Sn%	Sb%	Cr %	Co%	Au%	Ni %	Fe%	Pb%	As%	Cu %	Total
71	Tetricus I	E786		0.53	0.081	0.31	0.166	0.050	0.010	0.01	0.009	0.143	2.21	0.09	95.68	99.3
72	Tetricus I	E787		0.57	0.104	0.30	0.171	0.050	0.006	0.01	0.011	0.084	2.03	0.13	95.86	99.3
73	Tetricus I	E775		0.72	0.151	0.25	0.141	0.050	0.006	0.01	0.016	0.040	1.82	0.15	97.12	100.5
74	Tetricus I	E775		0.87	0.081	0.21	0.152	0.050	0.006	0.01	0.017	0.026	1.26	0.18	93.42	96.3
75	Tetricus II	E791		0.77	0.024	0.01	0.171	0.050	0.006	0.01	0.053	0.010	2.23	0.16	99.45	102.9
76	Tetricus II	E769		0.96	0.098	0.01	0.143	0.050	0.008	0.01	0.029	0.010	2.10	0.16	99.74	103.3
77	Tetricus II	E769		0.43	0.013	0.01	0.086	0.050	0.008	0.01	0.016	0.010	1.34	0.16	100.51	102.6
78	Tetricus II	E778		0.65	0.029	0.01	0.155	0.050	0.005	0.01	0.011	0.032	2.46	0.13	94.28	97.8
	"COPIES"															
79	Gallienus-sole	as RIC499		2.33	0.768	4.91	0.099	0.050	0.006	0.03	0.025	0.021	3.37	0.11	95.18	106.9
80	Claudius II	as RIC157		0.51	2.525	2.72	0.149	0.050	0.010	0.01	0.019	0.077	1.99	0.14	98.30	106.5
81	Postumus	as E299		0.71	0.025	2.48	0.068	0.050	0.006	0.01	0.012	0.007	2.55	0.21	97.30	103.4
82	unattributable			0.06	0.558	10.98	0.089	0.050	0.010	0.01	0.019	0.026	2.29	0.14	95.38	109.6

WALBOTTLE HOARD ANALYTICAL DATA (CONTINUED)

No.	RIC	Mint	Ag%	Pb%	Ni%	Fe%	Zn%	Au%	As%	Sb%	Co%	Cr%	Sn%	Cu%	Total
1	479	Trier	1.70	8.05	0.098	0.418	0.055	0.016	0.065	0.095	0.024	0.022	2.82	87.20	100.49
2	479	Trier	0.94	7.99	0.087	0.321	0.077	0.036	0.077	0.118	0.025	0.024	3.87	86.07	99.55
3	479	Trier	1.26	7.03	0.096	0.268	0.105	0.052	0.073	0.104	0.024	0.030	4.22	85.65	98.84
4	479	Trier	1.09	7.73	0.121	0.145	0.065	0.043	0.106	0.109	0.024	0.030	3.32	87.44	100.12
5	479	Trier	1.18	6.94	0.086	0.433	0.117	0.038	0.097	0.101	0.019	0.033	3.65	81.27	93.87
6	475	Trier	0.34	8.85	0.088	0.104	0.172	0.046	0.130	0.106	0.022	0.022	3.27	84.36	97.39
7	475	Trier	1.12	8.68	0.033	0.091	0.070	0.050	0.113	0.135	0.022	0.022	4.51	86.51	101.25
8	475	Trier	0.89	8.42	0.036	0.122	0.060	0.051	0.152	0.084	0.024	0.024	3.64	85.65	98.99
9	475	Trier	1.21	9.82	0.043	0.122	0.111	0.049	0.129	0.089	0.021	0.021	3.10	81.20	95.78
10	475	Trier	1.08	7.46	0.052	0.148	0.088	0.021	0.181	0.109	0.026	0.026	4.33	89.14	102.48
11	295	London	0.86	5.39	0.075	0.074	0.057	0.019	0.094	0.102	0.025	0.025	3.96	90.45	101.04
12	295	London	0.96	5.59	0.064	0.064	0.074	0.027	0.079	0.096	0.026	0.026	4.88	89.74	101.55
13	295	London	0.44	5.80	0.063	0.046	0.079	0.031	0.093	0.100	0.025	0.027	3.86	91.37	101.84
14	295	London	1.12	5.08	0.050	0.084	0.084	0.023	0.081	0.138	0.025	0.023	3.80	90.88	101.30
15	295	London	1.26	6.17	0.075	0.029	0.031	0.027	0.095	0.132	0.025	0.037	4.66	89.05	101.50
16	296	London	1.12	7.13	0.062	0.142	0.064	0.032	0.090	0.143	0.025	0.043	3.85	89.04	101.66
17	296	London	0.50	5.28	0.072	0.046	0.052	0.035	0.072	0.128	0.024	0.041	3.76	92.03	101.96,
18	296	London	1.07	5.47	0.071	0.028	0.034	0.031	0.063	0.097	0.024	0.046	3.67	87.50	98.04
19	296	London	1.09	6.19	0.062	0.031	0.086	0.041	0.112	0.121	0.025	0.056	3.63	91.54	102.88
20	296	London	1.18	6.03	0.082	0.040	0.060	0.031	0.116	0.121	0.023	0.058	4.06	87.56	99.25
21	449	Trier	0.75	7.61	0.049	0.321	0.127	0.012	0.080	0.113	0.025	0.027	3.91	89.83	102.77
22	213	Trier	2.11	1.53	0.037	0.083	0.032	0.025	0.063	0.088	0.025	0.030	1.40	92.45	97.81
23	213	Trier	1.91	3.09	0.030	0.140	0.146	0.028	0.066	0.113	0.020	0.026	2.91	86.13	94.55
24	224	Trier	0.22	3.78	0.053	0.130	0.175	0.015	0.088	0.108	0.026	0.032	4.30	93.68	102.52
25	213	Trier	1.40	1.73	0.050	0.272	0.027	0.047	0.092	0.082	0.050	0.084	1.73	102.48	107.96
26	148	Lyon	0.93	8.75	0.060	0.053	0.133	0.024	0.109	0.087	0.024	0.042	5.28	85.70	101.07
27	148	Lyon	0.37	6.50	0.062	0.059	0.088	0.020	0.080	0.103	0.025	0.006	5.11	90.10	102.44
28	148	Lyon	0.55	6.61	0.078	0.101	0.075	0.026	0.117	0.126	0.026	0.026	4.65	87.69	99.95
29	64	Aquilea	0.18	15.77	0.105	0.020	0.051	0.017	0.125	0.176	0.030	0.024	9.79	79.67	105.83
30	133	Lyon	0.16	8.47	0.049	0.092	0.097	0.021	0.107	0.139	0.025	0.028	4.82	87.81	101.70
31	133	Lyon	0.33	6.81	0.069	0.106	0.090	0.009	0.059	0.149	0.028	0.041	5.23	89.78	102.65
32	133	Lyon	0.85	7.68	0.048	0.062	0.068	0.009	0.052	0.124	0.024	0.024	4.80	87.86	101.54
33	133	Lyon	0.45	10.04	0.065	0.080	0.202	0.006	0.057	0.141	0.026	0.026	4.69	85.75	101.48
34	133	Lyon	0.25	7.30	0.067	0.113	0.270	-0.001	0.065	0.116	0.027	0.023	5.81	88.58	102.55
35	174	Lyon	0.70	7.22	0.083	0.135	0.082	0.003	0.110	0.136	0.028	0.026	5.15	89.72	103.29
36	14	Lyon	0.21	28.57	0.079	0.038	0.028	0.009	0.172	0.091	0.026	0.033	1.56	72.49	103.13
37	220	London	0.57	4.31	0.071	0.166	0.143	0.021	0.097	0.146	0.029	0.047	3.36	94.43	103.29

TINGRITH HOARD, INITIAL SET OF ANALYTICAL DATA

No.	Ref	Ag%	Pb%	Zn%	Sn%	As%	Ni%	Fe%	Au%	Sb%	Co%
1	96	1.017	6.815	0.028	2.817	0.211	0.047	0.030	0.027	0.219	0.033
2	195	0.076	2.015	0.020	5.025	0.222	0.043	0.058	0.022	0.144	0.081
4	215	0.729	9.005	0.184	4.726	0.082	0.048	0.092	0.023	0.106	0.025
5	221	0.873	3.831	0.110	3.425	0.069	0.045	0.076	0.031	0.142	0.025
6	247	0.842	5.125	0.027	3.324	0.126	0.064	0.050	0.024	0.163	0.080
7	302	1.160	5.901	0.125	3.720	0.139	0.071	0.068	0.030	1.531	0.054
9	412	1.027	3.221	0.076	2.626	0.141	0.024	0.136	0.027	0.165	0.034
10	1093	1.140	5.910	0.093	3.850	0.121	0.040	0.100	0.028	0.149	0.077
11	1125	1.425	4.970	0.303	3.964	0.274	0.033	0.180	0.031	0.190	0.056
12	1742	1.403	6.889	0.120	4.826	0.407	0.046	0.150	0.033	0.222	0.091
13	1951	0.080	8.589	0.184	4.458	0.131	0.024	0.025	0.014	0.113	0.084

TINGRITH HOARD, 'ODD' COIN ANALYSES (Chromium and copper not analysed)

Cat.No.	No.	Pb%	Sn%	Au%	Zn%	Ni%	Fe%	Ag%	Co%	Sb%	Cr%	As%	Cu%	Total
Beata Tranquillitas RIC368														
448	1	9.34	3.029	0.035	0.051	0.042	0.492	0.649	0.035	0.203	0.070	0.192	87.25	101.39
449	2	10.07	2.815	0.035	0.040	0.037	0.157	0.623	0.025	0.188	0.046	0.389	85.49	99.92
451	3	12.33	3.137	0.038	0.070	0.047	0.079	0.983	0.028	0.242	0.098	0.094	84.70	101.85
452	4	11.76	3.401	0.037	0.050	0.048	0.217	0.680	0.024	0.219	0.067	0.093	86.64	103.23
453	5	5.34	4.322	0.036	0.175	0.064	0.127	0.599	0.002	0.244	0.116	0.089	93.21	104.33
454	6	6.77	5.180	0.032	0.167	0.036	0.270	0.560	0.021	0.091	0.062	0.299	88.14	101.63
456	7	6.18	2.926	0.033	0.029	0.033	0.267	0.729	0.028	0.115	0.085	0.193	89.88	100.50
457	8	8.64	4.379	0.033	0.050	0.042	0.300	0.558	0.035	0.133	0.140	0.231	88.17	102.71
459	9	13.46	3.012	0.033	0.046	0.036	0.118	0.569	0.013	0.080	0.057	0.167	86.28	103.87
463	10	8.40	4.478	0.048	0.245	0.041	0.219	0.775	0.031	0.106	0.063	0.291	88.40	103.09
Caesarum Nostrorum RIC441														
1794	11	18.07	3.201	0.034	0.037	0.044	1.113	0.974	0.032	0.129	0.083	0.309	78.41	102.44
1795	12	9.32	4.924	0.037	0.067	0.052	0.264	0.501	0.006	0.124	0.102	0.370	87.06	102.82
1796	13	11.44	4.138	0.038	0.248	0.049	0.588	0.533	0.013	0.146	0.064	0.497	85.09	102.84
1797	14	12.41	3.721	0.033	0.041	0.048	0.309	0.851	0.013	0.146	0.050	0.083	85.37	103.08
1798	15	11.91	3.979	0.034	0.135	0.051	0.488	0.702	0.014	0.170	0.065	0.086	82.49	100.12
1799	16	16.84	3.068	0.033	0.031	0.036	0.526	0.644	0.031	0.119	0.078	0.205	80.61	102.22
1800	17	11.52	3.740	0.034	0.068	0.036	0.152	0.592	0.030	0.145	0.093	0.244	84.51	101.16
1801 top	18	15.90	2.712	0.033	0.069	0.035	0.470	0.611	0.038	0.116	0.020	0.293	82.31	102.61
1801 bottom	19	14.89	3.010	0.034	0.072	0.035	0.487	0.558	0.017	0.116	0.024	0.288	82.99	102.52
1802	20	16.32	2.727	0.033	0.041	0.036	0.408	0.678	0.021	0.136	0.050	0.150	82.87	103.47
1804	21	13.77	2.168	0.036	0.088	0.036	0.238	0.505	0.018	0.161	0.045	0.179	84.93	102.17

TINGRITH HOARD, TWO ISSUES FOR COMPARISON WITH RICHBOROUGH DATA.

No.	Issue	Mint	Sn %	Pb %	Ag %	Zn %	Ni %	Fe %	As %	Co %	Cr %
1	Cons.II.Prov.Caess	Trier	1.44	13.17	1.21	0.08	0.04	0.59	0.29	0	0.13
6	Constantinopolis	Trier	4.07	7.99	0.91	0.04	0.04	0.57	0.26	0.01	0.14
11	Constantinopolis	Trier	2.41	17.99	1.06	0.03	0.05	0.55	0.31	0	0.18
12	Constantinopolis	Trier	1.68	13.92	0.78	0.03	0.04	0.76	0.28	0.01	0.15
16	Urbs Roma	Trier	2.63	18.57	1.02	0.05	0.05	0.22	0.14	0.01	0.28
23	Cons.II.Glor.Ex.	Trier	1.85	9.41	0.98	0.02	0.06	0.38	0.12	0.01	0.28
24	Constantius II.G.Ex	Trier	4.85	11.22	0.81	0.03	0.04	1.06	0.05	0.01	0.3
26	Constantinopolis	Trier	1.91	8.31	0.87	0.02	0.05	0.31	0.1	0.01	0.05
32	Urbs Roma	Trier	2.52	11.64	0.9	0.05	0.06	0.44	0.07	0.01	0.09
39	Cons.II.Glor.Ex.	Lyons	1.48	10.92	0.74	0.03	0.15	0.59	0.41	0.04	0.14
40	Urbs Roma	Lyons	1.5	8.33	0.8	0.04	0.12	0.37	0.41	0.04	0.2
43	Cons.II.Glor.Ex.	Lyons	1.63	11.91	0.78	0.03	0.12	0.37	0.43	0.04	0.16
44	Constantius II.G.Ex	Lyons	3.19	15.63	0.76	0.05	0.05	1.17	0.22	0.03	0.19
45	Cons.II.Glor.Ex.	Lyons	1.56	17.79	0.68	0.02	0.04	0.65	0.1	0.01	0.21
46	Cons.II.Glor.Ex.	Lyons	1.72	7.4	0.56	0.02	0.04	0.05	0.07	0.01	0.21
52	Urbs Roma	Arles	1.4	24.28	0.58	0.01	0.05	0.06	0.14	0.02	0.07
61	Urbs Roma	Copy	2.32	26.96	0.13	0.3	0.04	0.05	0.04	0.01	0.07
68	Cons.I.Glor.Ex.	Copy	0.46	29.55	0.11	0	0.04	0.02	0.14	0.01	0.11
69	Cons.II.Glor.Ex.	Copy	0.67	17.68	0.19	0	0.04	0.01	0.09	0.01	0.08
70	Cons.II.Glor.Ex.	Copy	1.43	15.5	0.25	0.04	0.04	0.01	0.11	0.01	0.11
71	Constantinopolis	Copy	2.11	18.25	0.16	0.01	0.05	0.04	0.1	0.01	0.05
76	Urbs Roma	Copy	2.23	19.21	0.09	0.96	0.06	0.14	0.14	0.02	0.03

BANCROFT HOARD ANALYTICAL DATA

(Antimony and copper not analysed)

No.	Ag%	As%	Au%	Co%	Cr%	Fe%	Ni%	Pb%	Sb%	Sn%	Zn%	Cu%	Total
1	1.73	0.098	0.041	0.039	0.074	0.065	0.049	6.09	0.112	2.24	0.014	85.69	96.24
2	1.37	0.119	0.036	0.048	0.048	0.083	0.041	15.15	0.117	2.18	0.012	78.09	97.29
3	0.52	0.087	0.02	0.034	0.04	0.01	0.037	15.15	0.109	1.18	0.013	74.89	92.08
4	1.01	0.297	0.041	0.041	0.073	0.063	0.053	1.83	0.222	2.03	0.012	89.58	95.25
5	0.53	0.258	0.04	0.035	0.067	0.019	0.037	16.21	0.13	1.53	0.014	72.71	91.58
6	0.86	0.486	0.031	0.042	0.071	0.044	0.042	13.94	0.127	1.84	0.019	79.65	97.16
7	0.93	0.437	0.067	0.042	0.075	0.063	0.044	16.23	0.086	1.8	0.015	76.36	96.15
8	1.03	0.491	0.04	0.05	0.073	0.136	0.048	10.65	0.159	2.38	0.02	85.01	100.08
9	1.45	0.498	0.052	0.062	0.105	0.092	0.068	10.23	0.188	2.16	0.022	89.88	104.81
10	0.96	0.417	0.04	0.045	0.085	0.101	0.04	18.01	0.175	2.93	0.038	73.17	96.01
11	1.03	0.426	0.045	0.036	0.036	0.761	0.05	4.41	0.163	1.81	0.018	61	69.77
12	0.98	0.433	0.034	0.048	0.048	0.082	0.048	0.73	0.176	0.83	0.01	90.55	93.97
13	1.39	0.492	0.051	0.046	0.046	0.116	0.039	9.39	0.169	2.61	0.012	78.76	93.12
14	0.7	0.371	0.043	0.039	0.039	0.051	0.045	9.92	0.146	1.63	0.014	74.64	87.63
14A	1	0.381	0.051	0.046	0.046	0.081	0.049	14.34	0.105	1.83	0.014	77.24	95.19
15	1.01	0.198	0.032	0.032	0.032	0.096	0.04	12.6	0.136	2.87	0.042	76.73	93.82
16	1.28	0.278	0.028	0.043	0.043	0.117	0.063	2.76	0.267	1.95	0.011	87.55	94.39
17	0.61	0.174	0.021	0.028	0.028	0.242	0.041	7.79	0.151	1.81	0.027	79.46	90.38
18	0.97	0.079	0.031	0.031	0.031	0.056	0.048	10.49	0.17	1.87	0.017	77.99	91.78
19	1.62	0.12	0.043	0.048	0.05	0.101	0.058	5.53	0.199	2.19	0.022	82.46	92.44
20	1.7	0.139	0.041	0.03	0.033	0.05	0.044	6.4	0.144	1.97	0.017	78.67	89.23

STONEYKIRK HOARD ANALYTICAL DATA

No.	Zn%	As%	Au%	Co%	Cr %	Sb%	Ag%	Sn%	Pb%	Fe%	Ni%	Cu%	Total
1	0.006	0.043	0.026	0.043	0.045	0.043	0.162	0.51	17.054	0.189	0.055	77.61	95.787
2	0.014	0.285	0.045	0.043	0.043	0.045	0.387	1.65	5.263	0.048	0.094	86.85	94.765
3	0.038	0.106	0.033	0.045	0.081	0.034	0.5	2.8	14.318	0.453	0.063	75.97	94.434
4	0.014	0.042	0.034	0.04	0.04	0.024	0.655	1.35	17.127	0.526	0.082	65.18	85.107
5	0.019	0.163	0.042	0.045	0.045	0.032	0.342	2.18	14.73	0.41	0.066	73.78	91.854
6	0.687	0.035	0.021	0.006	0.042	0.096	0.107	6.75	14.325	0.246	0.067	69.52	91.899
7	0.048	0.057	0.009	0.011	0.016	0.095	0.508	3.21	8.81	0.135	0.099	79.9	92.901
8	0.012	0.19	0.007	0.031	0.014	0.086	0.541	1.09	6.431	0.7	0.08	81.86	91.037
9	0.015	0.032	0.033	0.032	0.01	0.163	1.043	0.27	1.516	0.082	0.087	90.53	93.817
10	2.008	0.034	0.009	0.034	0.012	0.044	0.076	4.73	9.6	0.201	0.064	78	94.813
11	0.017	0.054	0.025	0.032	0.008	0.032	0.446	1.54	13.424	0.625	0.041	78.89	95.131
12	0.012	0.045	0.025	0.045	0.02	0.034	0.708	0.15	25.11	0.295	0.049	65.76	92.247
13	0.026	0.037	0.038	0.037	0.019	0.06	0.43	1.84	7.541	0.396	0.076	77.45	87.952
14	1.039	0.063	0.037	0.063	0.063	0.216	0.136	7.94	16.793	0.365	0.041	68.78	95.537
15	0.025	0.13	0.034	0.029	0.021	0.068	0.598	2.23	17.544	0.424	0.036		
16	0.036	0.067	0.016	0.048	0.091	1.107	1.28	7.17	5.361	0.38	0.031	76.79	92.374
17	0.018	0.249	0.014	0.027	0.061	0.11	0.423	2.81	14.248	0.44	0.013	75.83	94.245
18	0.027	0.09	0.019	0.05	0.09	0.118	1.058	5.66	17.828	0.438	0.693	74.15	100.217
19	2.314	0.036	0.005	0.036	0.023	0.164	0.068	2.04	2.764	0.172	0.05	88.9	96.577
20	0.013	0.041	0.019	0.041	0.028	0.093	0.684	0.07	1.807	0.114	0.035	86.13	89.072
21	0.016	0.04	0.033	0.04	0.044	0.067	0.585	2.55	21.897	2.123	0.018	49.19	76.609
22	0.051	0.045	0.025	0.045	0.047	0.077	0.795	3.2	12.822	0.763	0.074	78.84	96.784
23	0.036	0.083	0.192	0.083	0.083	0.083	4.088	0.74	0.176	0.265	0.309	63.64	69.778
24	0.013	0.043	0.038	0.043	0.039	0.021	0.096	1.58	22.12	0.127	0.038	59.59	83.74
25	0.023	0.04	0.041	0.04	0.046	0.067	0.479	2.29	21.488	0.117	0.062	63.58	88.272
26	0.018	0.044	0.022	0.044	0.044	0.044	0.2	0.29	44.829	0.041	0.159	52.95	98.694
27	0.018	0.045	0.005	0.045	0.067	0.076	0.976	0.22	1.432	0.114	0.07	92.45	95.519
28	0.022	0.04	0.022	0.04	0.059	0.081	0.79	5.48	1.37	0.082	0.059	88.26	96.304

MARKET DEEPING ANALYTICAL DATA

No.	Ag%	Au%	As%	Ni%	Pb%	Sn%	Zn%	Fe%	Sb%	Cr%	Co%
r1	0.65	0.390	0.296	0.029	8.79	2.30	0.060	0.570	0.100	0.143	0.020
r2	1.88	0.001	0.451	0.030	4.89	2.12	0.089	0.251	0.057	0.155	0.027
r4	0.79	0.020	0.398	0.034	9.70	2.79	0.098	0.586	0.060	0.185	0.022
r5	0.64	0.001	0.406	0.026	9.95	2.47	0.116	0.412	0.020	0.196	0.030
r6	0.70	0.010	0.232	0.040	2.81	2.91	0.072	0.278	0.060	0.060	0.028
r7	0.77	0.030	0.094	0.050	8.59	3.64	0.077	0.140	0.057	0.041	0.016
r8	0.86	0.030	0.078	0.043	6.08	3.44	0.065	0.123	0.020	0.047	0.010
r9	1.30	0.080	0.105	0.050	4.93	3.29	0.060	0.126	0.063	0.063	0.017
r10	0.63	0.060	0.197	0.043	9.24	3.29	0.066	0.329	0.052	0.052	0.015
r11	0.88	0.050	0.252	0.035	5.18	3.44	0.050	0.137	0.071	0.071	0.023
r12	0.62	0.040	0.117	0.039	3.94	3.33	0.058	0.741	0.055	0.055	0.015
r13	0.62	0.070	0.121	0.026	4.08	3.59	0.053	0.086	0.074	0.074	0.017
r14	1.07	0.070	0.169	0.030	7.71	2.98	0.087	0.256	0.040	0.064	0.010
r15	0.55	0.080	0.224	0.026	5.70	3.44	0.049	0.660	0.055	0.055	0.027
r16	0.63	0.030	0.109	0.024	4.41	3.26	0.048	0.137	0.066	0.086	0.021
r17	0.87	0.020	0.134	0.033	6.70	4.46	0.059	0.094	0.080	0.070	0.020
r18	0.59	0.050	0.029	0.027	6.68	3.73	0.050	0.450	0.062	0.062	0.027
r19	0.67	0.070	0.265	0.026	5.48	3.42	0.061	0.190	0.074	0.074	0.026
r20	0.76	0.010	0.325	0.032	12.62	2.90	0.037	0.115	0.020	0.072	0.030
r21	0.62	0.001	0.655	0.029	6.74	3.61	0.040	0.522	0.073	0.073	0.022
r22	0.73	0.040	0.231	0.029	1.94	3.78	0.069	0.109	0.075	0.075	0.021
r23	0.72	0.060	0.496	0.034	4.51	4.37	0.035	0.116	0.030	0.074	0.030
r24t	0.70	0.040	0.127	0.088	3.97	4.18	0.033	0.163	0.077	0.077	0.015
r25	0.67	0.030	0.089	0.046	5.25	2.88	0.023	0.018	0.050	0.054	0.020
r26	0.58	0.030	0.071	0.037	7.14	3.06	0.039	0.577	0.053	0.053	0.018
r30	1.56	0.050	0.227	0.034	4.55	4.15	0.065	0.534	0.170	0.170	0.019
r31	0.56	0.030	0.095	0.038	6.35	3.93	0.103	0.091	0.057	0.057	0.018
r32	0.74	0.030	0.069	0.040	6.18	4.75	0.112	0.477	0.067	0.067	0.017
r33	0.68	0.030	0.105	0.034	6.15	3.54	0.052	0.088	0.109	0.071	0.015
r34	0.95	0.040	0.122	0.029	5.31	3.34	0.101	0.119	0.090	0.122	0.020
r35	0.62	0.040	0.092	0.034	6.64	3.94	0.041	0.608	0.071	0.056	0.014
r36	0.70	0.040	0.102	0.033	13.26	3.45	0.153	0.289	0.063	0.061	0.015
r37	0.98	0.040	0.101	0.042	6.39	3.04	0.055	0.119	0.050	0.061	0.020
r38	0.63	0.040	0.095	0.025	4.11	4.30	0.055	0.474	0.084	0.057	0.008
r41	0.64	0.050	0.115	0.041	3.13	3.37	0.054	0.092	0.074	0.069	0.009
r42	0.47	0.040	0.091	0.024	5.40	3.17	0.084	0.186	0.070	0.055	0.010
r43	0.86	0.080	0.101	0.040	5.21	4.05	0.078	0.530	0.071	0.060	0.010
r44	0.98	0.020	0.292	0.039	5.34	3.93	0.127	0.299	0.085	0.071	0.008
r45	0.60	0.050	0.077	0.037	9.82	5.76	0.075	0.121	0.069	0.073	0.010
r46	0.44	0.050	0.082	0.023	7.90	4.54	0.046	0.103	0.108	0.077	0.009
r47	0.79	0.060	0.122	0.041	7.96	3.50	0.050	0.071	0.073	0.073	0.009
r48	0.51	0.050	0.118	0.026	3.40	4.51	0.042	0.126	0.064	0.071	0.010
r49	0.64	0.040	0.109	0.033	2.66	1.86	0.020	0.539	0.065	0.083	0.007
r50	0.61	0.020	0.100	0.030	4.57	3.71	0.099	0.569	0.060	0.060	0.008
r51	0.72	0.030	0.127	0.037	3.02	3.97	0.095	0.060	0.090	0.065	0.010
r53	0.90	0.030	0.124	0.027	4.29	3.19	0.081	0.141	0.063	0.073	0.006
r54	1.25	0.030	0.163	0.028	4.69	3.21	0.106	0.460	0.084	0.060	0.010
r55	0.65	0.030	0.104	0.037	7.50	3.94	0.041	0.042	0.060	0.053	0.010
r56	0.75	0.030	0.130	0.033	10.12	4.48	0.063	0.229	0.060	0.071	0.008
r57	0.93	0.020	0.320	0.041	6.34	3.80	0.039	0.232	0.065	0.069	0.009
r58	0.80	0.020	0.366	0.048	4.57	3.66	0.043	0.260	0.080	0.118	0.010
r59	0.79	0.020	0.363	0.041	3.75	3.81	0.044	0.421	0.065	0.115	0.010
r60	0.75	0.030	0.357	0.038	2.92	3.64	0.087	0.222	0.057	0.057	0.010
r61	0.96	0.020	0.116	0.065	2.15	1.09	0.024	0.259	0.250	0.069	0.010
r62	0.86	0.030	0.099	0.038	1.53	3.18	0.043	0.218	0.060	0.060	0.010
r63	0.78	0.020	0.109	0.100	2.53	2.10	0.037	0.288	0.065	0.065	0.010
r64	0.58	0.020	0.078	0.034	4.26	2.55	0.033	0.241	0.060	0.047	0.010
r66	0.79	0.030	0.259	0.044	3.01	4.71	0.045	0.246	0.060	0.055	0.010
r67	0.81	0.030	0.323	0.080	3.32	0.81	0.018	0.198	0.057	0.043	0.010
r68	0.84	0.030	0.313	0.024	2.18	2.59	0.063	0.186	0.058	0.065	0.010
r69	0.72	0.030	0.398	0.038	12.14	3.45	0.036	0.258	0.054	0.064	0.010
r70	1.02	0.030	0.372	0.033	3.46	2.46	0.045	0.131	0.058	0.061	0.010
r71	0.98	0.030	0.449	0.037	5.64	4.54	0.041	0.033	0.061	0.059	0.010
r72	0.65	0.030	0.391	0.036	12.61	3.32	0.030	0.250	0.060	0.043	0.010
r73	0.87	0.030	0.098	0.037	4.14	4.64	0.049	0.065	0.064	0.059	0.010
r74	0.99	0.030	0.117	0.035	5.11	3.69	0.049	0.021	0.110	0.070	0.010
r75	0.91	0.030	0.123	0.034	7.00	3.47	0.041	0.039	0.074	0.094	0.010
r76	0.59	0.030	0.088	0.039	6.67	3.32	0.045	0.222	0.053	0.064	0.010
r77	0.69	0.030	0.140	0.030	3.84	4.31	0.047	0.078	0.090	0.091	0.010
r78	0.71	0.020	0.303	0.019	8.51	2.33	0.031	0.123	0.064	0.105	0.010
r79	0.84	0.020	0.310	0.029	3.27	3.28	0.022	0.021	0.080	0.103	0.010
r80	0.97	0.010	0.420	0.067	5.04	2.63	0.025	0.023	0.090	0.147	0.010
r81	0.79	0.020	0.319	0.030	5.03	3.93	0.039	0.175	0.087	0.085	0.010

RICHBOROUGH LUMP ANALYSES.

Appendix 3.

Blank No.12		Blank No.12: the lead globule
Cu K	77.138	11.396
S K	0.37	7.719
Fe K	0.798	0.149
Sn L	4.329	0.135
As K	0.584	5.366
Zn K	1.035	0.184
Pb L	2.072	73.213
Ag L	0.955	1.792
Total	87.28	99.954

Pellet No.47	
Cu K	87.14
S K	0.34
Fe K	0.686
Sn L	8.04
As K	3.792
Zn K	0
Total	100

Surface of Blank No.5		Surface of Blank No.19
Cu K	8.829	18.429
Al K	0.178	0.526
Si K	1.192	1.537
Fe K	17.87	6.416
Pb L	7.392	6.724
Ca K	0.29	1.307
P K	0.917	1.578
S K	0.786	0.752
Zn K		0.761
Total	37.453	38.031

FENNY STRATFORD QUANTITATIVE EDAX ANALYSES

Electron Micro-probe quantative analysis data.

Point	Ag	Ni	Fe	Sn	As	Pb
1a	1.022	0.032	0.018	3.941	0	0.099
1b	1.103	0.031	0.034	4.084	0	0.233
1c	1.056	0.038	0.015	3.997	0.116	0.115
1	1.06	0.034	0.022	4.007	0.039	0.149
2a	1.119	0.046	0.005	4.145	0.283	0.14
2b	1.071	0.051	0.016	4.025	0.582	0.209
2c	0.908	0.04	0.013	3.997	0	0.136
2	1.033	0.046	0.011	4.056	0.288	0.161
3a	0.908	0.036	0.018	3.893	0.576	0.116
3b	0.9	0.053	0.017	3.897	0.663	0.025
3c	0.919	0.025	0.017	3.891	0.47	0.21
3	0.909	0.038	0.018	3.893	0.57	0.117
4a	1.016	0.042	0.003	4.081	0.237	0.071
4b	1.035	0.025	0.016	4.198	0.543	0.212
4c	0.984	0.027	0.02	4.06	0.14	0.125
4	1.012	0.031	0.013	4.113	0.306	0.136
5a	0.875	0.036	0.029	3.928	0.13	0.145
5b	0.892	0.047	0.026	3.93	0.317	0.215
5c	0.864	0.045	0.021	3.87	0.161	0.122
5	0.877	0.043	0.025	3.91	0.203	0.161
6a	0.828	0.007	0.025	3.578	0.409	0.138
6b	0.808	0.051	0.016	3.541	0	0.204
6c	0.774	0.034	0.013	3.605	0	0.167
6	0.803	0.031	0.018	3.575	0.136	0.17
7a	0.912	0.018	0.015	3.953	0	0.152
7b	0.871	0.04	0.014	3.816	0.206	0.088
7c	0.932	0.032	0.008	4.047	0.125	0.18
7	0.905	0.03	0.012	3.939	0.11	0.14
8a	1.131	0.034	0	4.054	0.201	0.225
8b	1.166	0.032	0.013	4.221	0.565	0.16
8c	1.073	0.039	0.035	4.204	0.11	0.249
8	1.123	0.035	0.016	4.159	0.292	0.211
9a	1.09	0.066	0.025	4.105	0.473	0.196
9b	1.229	0.013	0.01	4.346	0.387	0.114
9c	1.186	0.069	0	4.248	0.366	0.165
9	1.168	0.049	0.011	4.233	0.409	0.158
10a	1.201	0.013	0	4.254	0.385	0.14
10b	1.01	0.031	0.001	4.038	0.263	0.157
10c	1.288	0.034	0.005	4.309	0.038	0.141
10	1.166	0.026	0.002	4.2	0.229	0.146
11a	1.248	0.036	0.094	3.118	0.181	0.442
11b	1.371	0.038	0.066	3.653	0.184	0.443
11c	1.332	0	0.018	3.868	0	0.58
11	1.317	0.025	0.059	3.546	0.122	0.488
12a	0.013	0.045	0.048	0.151	0.369	1.002
12b	0.032	0.046	0.016	0.183	0.156	1.251
12c	0.02	0.041	0.018	0.165	0	1.278
12	0.022	0.044	0.027	0.166	0.175	1.177

QUANTITATIVE POINT ANALYSIS FOR WALBOTTLE SAMPLE NO.28

Point	Ag	Ni	Fe	Sn	As	Pb
1a	1.022	0.032	0.018	3.941	0	0.099
1b	1.103	0.031	0.034	4.084	0	0.233
1c	1.056	0.038	0.015	3.997	0.116	0.115
1	1.06	0.034	0.022	4.007	0.039	0.149
2a	1.119	0.046	0.005	4.145	0.283	0.14
2b	1.071	0.051	0.016	4.025	0.582	0.209
2c	0.908	0.04	0.013	3.997	0	0.136
2	1.033	0.046	0.011	4.056	0.288	0.161
3a	0.908	0.036	0.018	3.893	0.576	0.116
3b	0.9	0.053	0.017	3.897	0.663	0.025
3c	0.919	0.025	0.017	3.891	0.47	0.21
3	0.909	0.038	0.018	3.893	0.57	0.117
4a	1.016	0.042	0.003	4.081	0.237	0.071
4b	1.035	0.025	0.016	4.198	0.543	0.212
4c	0.984	0.027	0.02	4.06	0.14	0.125
4	1.012	0.031	0.013	4.113	0.306	0.136
5a	0.875	0.036	0.029	3.928	0.13	0.145
5b	0.892	0.047	0.026	3.93	0.317	0.215
5c	0.864	0.045	0.021	3.87	0.161	0.122
5	0.877	0.043	0.025	3.91	0.203	0.161
6a	0.828	0.007	0.025	3.578	0.409	0.138
6b	0.808	0.051	0.016	3.541	0	0.204
6c	0.774	0.034	0.013	3.605	0	0.167
6	0.803	0.031	0.018	3.575	0.136	0.17
7a	0.912	0.018	0.015	3.953	0	0.152
7b	0.871	0.04	0.014	3.816	0.206	0.088
7c	0.932	0.032	0.008	4.047	0.125	0.18
7	0.905	0.03	0.012	3.939	0.11	0.14
8a	1.131	0.034	0	4.054	0.201	0.225
8b	1.166	0.032	0.013	4.221	0.565	0.16
8c	1.073	0.039	0.035	4.204	0.11	0.249
8	1.123	0.035	0.016	4.159	0.292	0.211
9a	1.09	0.066	0.025	4.105	0.473	0.196
9b	1.229	0.013	0.01	4.346	0.387	0.114
9c	1.186	0.069	0	4.248	0.366	0.165
9	1.168	0.049	0.011	4.233	0.409	0.158
10a	1.201	0.013	0	4.254	0.385	0.14
10b	1.01	0.031	0.001	4.038	0.263	0.157
10c	1.288	0.034	0.005	4.309	0.038	0.141
10	1.166	0.026	0.002	4.2	0.229	0.146
11a	1.248	0.036	0.094	3.118	0.181	0.442
11b	1.371	0.038	0.066	3.653	0.184	0.443
11c	1.332	0	0.018	3.868	0	0.58
11	1.317	0.025	0.059	3.546	0.122	0.488
12a	0.013	0.045	0.048	0.151	0.369	1.002
12b	0.032	0.046	0.016	0.183	0.156	1.251
12c	0.02	0.041	0.018	0.165	0	1.278
12	0.022	0.044	0.027	0.166	0.175	1.177

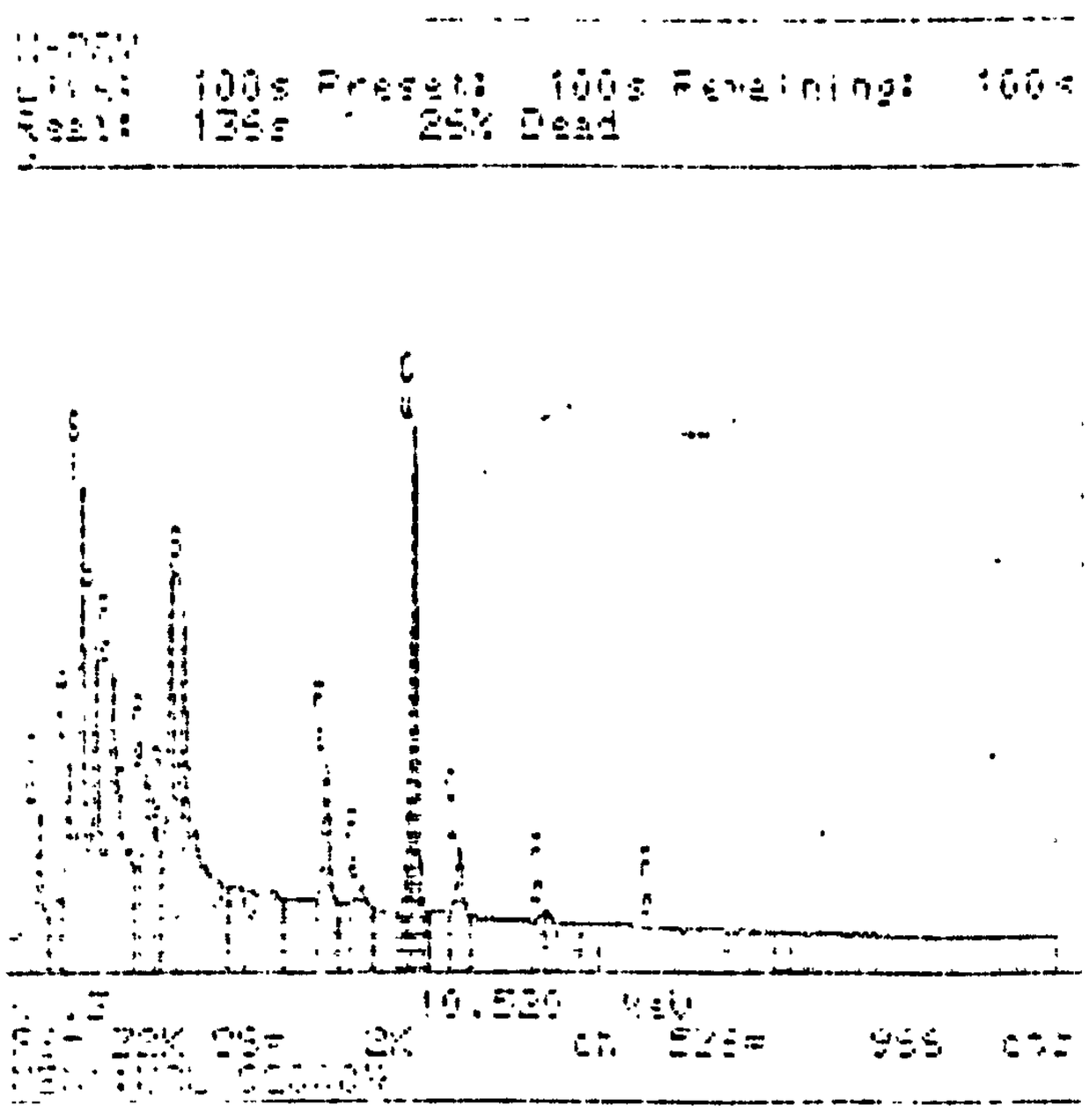
QUANTITATIVE POINT ANALYSIS FOR WALBOTTLE SAMPLE NO.30

Point	Ag	Ni	Fe	Sn	As	Pb
1a	0.002	0	0.037	0.013	0.299	0.269
1b	1.037	0.038	0.127	0.032	0.59	0.291
1c	1.061	0	0.101	0.059	0.202	0.283
1	0.7	0.013	0.089	0.035	0.364	0.281
2a	1.201	0.005	0.117	0.073	0.026	0.164
2b	1.157	0.031	0.16	0.09	0.189	0.145
2c	1.313	0	0.108	0.088	0	0.275
2	1.224	0.012	0.128	0.083	0.071	0.194
3a	1.143	0.03	0.131	0.09	0	0.075
3b	1.174	0	0.137	0.094	0.297	0.184
3c	1.204	0.01	0.132	0.093	0.069	0.076
3	1.174	0.013	0.133	0.092	0.122	0.112
4a	1.363	0	0.114	0.098	0.013	0.111
4b	1.324	0	0.124	0.097	0.593	0.056
4c	1.265	0.013	0.079	0.112	0.926	0.044
4	1.317	0.004	0.106	0.102	0.51	0.07
5a	1.253	0.007	0.141	0.052	0.055	0.247
5b	1.119	0.042	0.134	0.074	0	0.096
5c	1.204	0.015	0.141	0.049	0.038	0.12
5	1.192	0.021	0.139	0.059	0.031	0.154
6a	1.414	0.022	0.136	0.036	0.612	0.172
6b	1.344	0.036	0.139	0.046	0.385	0.104
6c	1.614	0.013	0.143	0.045	0.496	0.13
6	1.457	0.024	0.139	0.042	0.498	0.135
7a	0.981	0	0.18	0.118	0	2.453
7b	2.581	0	0.333	0.261	0	2.39
7c	2.566	0.016	0.333	0.285	0	2.362
7	2.043	0.005	0.282	0.221	0	2.402

QUANTITATIVE POINT ANALYSIS FOR WALBOTTLE SAMPLE NO.62

	Ag	Sn	Pb	Ni	Fe	As
2a	1.091	0.043	0.224	0.041	0.065	0.155
2b	0.774	0.076	0.424	0	0.07	0.435
2c	0.851	0.085	0.236	0	0.107	0.872
2	0.905	0.068	0.295	0.014	0.081	0.487
3a	0.658	0.088	0.85	0	0.144	0.089
3b	0.618	0.014	0.424	0	0.07	0.387
3c	0.814	0.089	0.075	0	0.069	0.647
3	0.697	0.064	0.45	0	0.094	0.374
4a	0.545	0.001	0	0.035	0.088	1.051
4b	0.625	0.041	1.226	0.006	0.083	0
4c	0.665	0.079	0	0.022	0.054	0.051
4	0.612	0.04	0.409	0.021	0.075	0.367
5a	0.636	0.046	0	0.022	0.087	0.353
5b	0.559	0	0	0.036	0.095	0
5c	0.62	0	0.052	0.044	0.069	0
5	0.605	0.015	0.017	0.034	0.084	0.118
6a	1.444	0.205	0.987	0.031	0.047	0.772
6b	1.321	0.122	0.805	0	0.141	0.074
6c	1.246	0.161	0.349	0	0.122	0
6	1.337	0.163	0.714	0.01	0.103	0.282
7a	0.697	0.054	0.481	0	0.06	0
7b	0.743	0.101	0.587	0.017	0.083	0
7	0.72	0.078	0.534	0.009	0.072	0
8a	0.849	0.082	1.194	0	0.067	0.532
8b	0.966	0.1	0.951	0	0.061	0.149
8	0.908	0.091	1.073	0	0.064	0.341
9a	1.423	0.18	1.427	0.036	0.135	0.459
9b	1.366	0.154	1.557	0.011	0.071	0.127
9	1.395	0.167	1.492	0.024	0.103	0.293
10a	1.361	0.153	0.589	0.03	0.132	0.946
10b	1.173	0.07	0.497	0	0.071	0
10	1.267	0.112	0.543	0.015	0.102	0.473

QUANTITATIVE POINT ANALYSIS FOR WALBOTTLE SAMPLE NO.68



EDAX SPECTRUM FOR THE SURFACE OF MKT.DEEPING NO.70 (A RADIATE COPY, SAMPLE NO.16).

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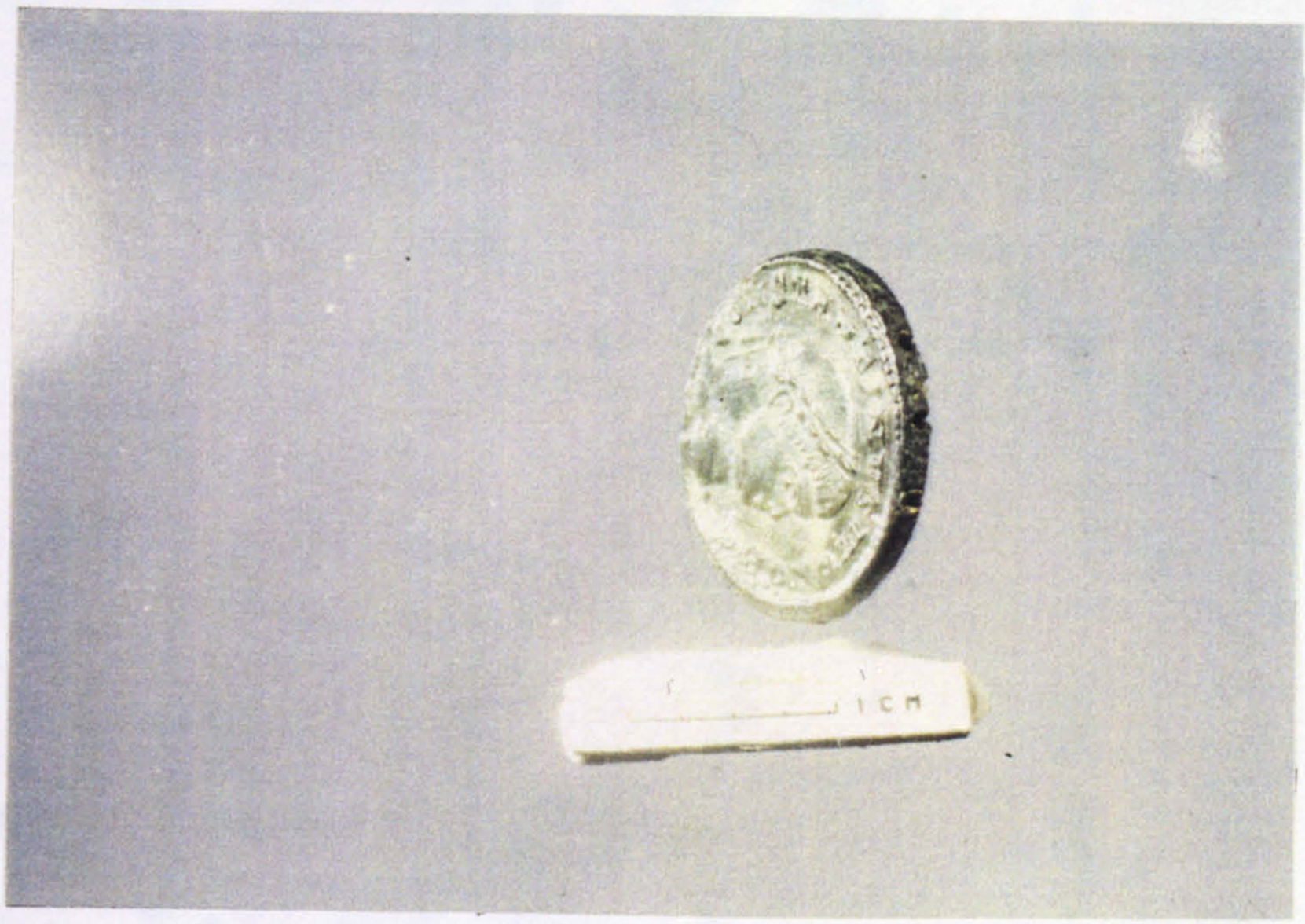

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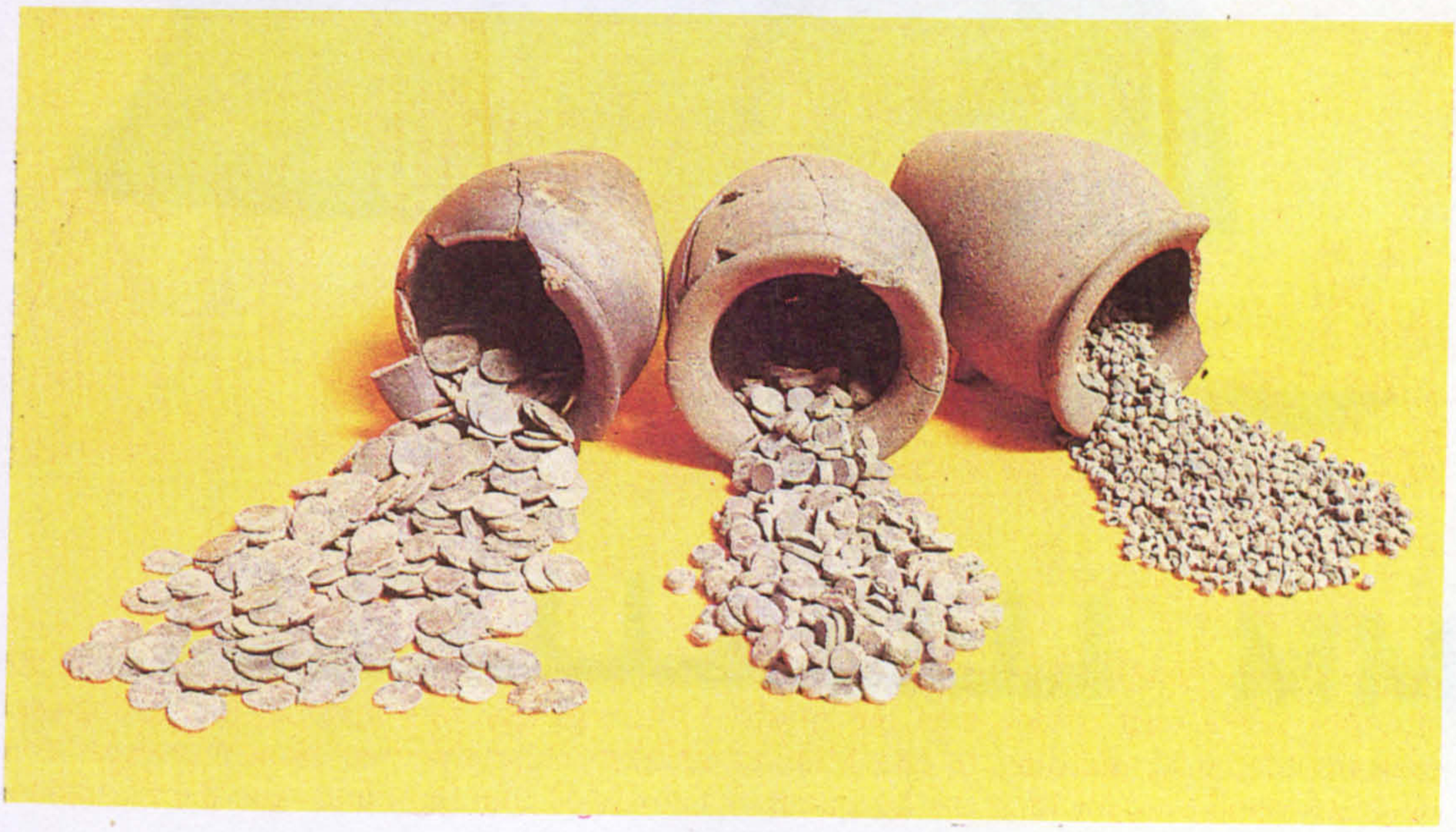

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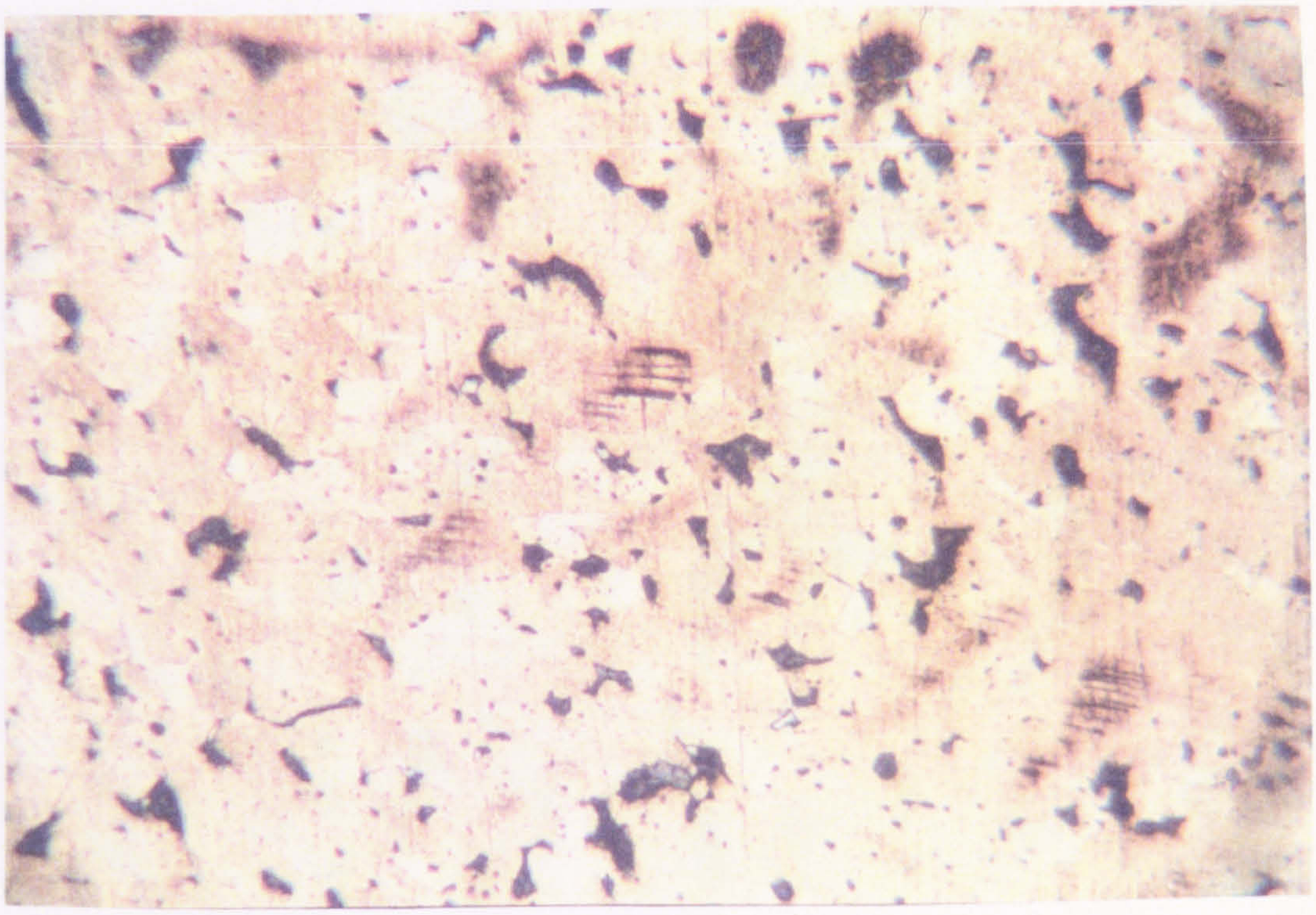

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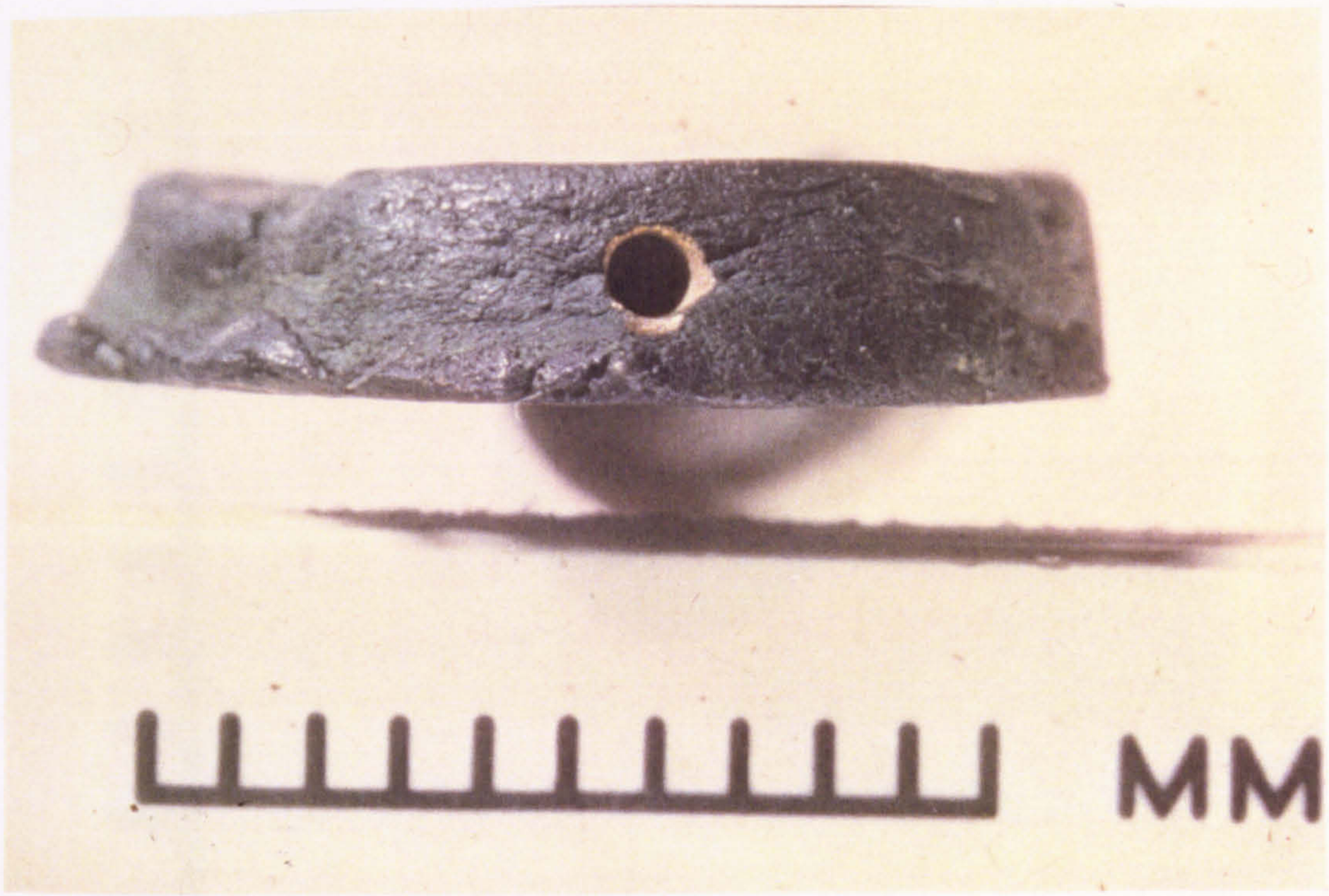

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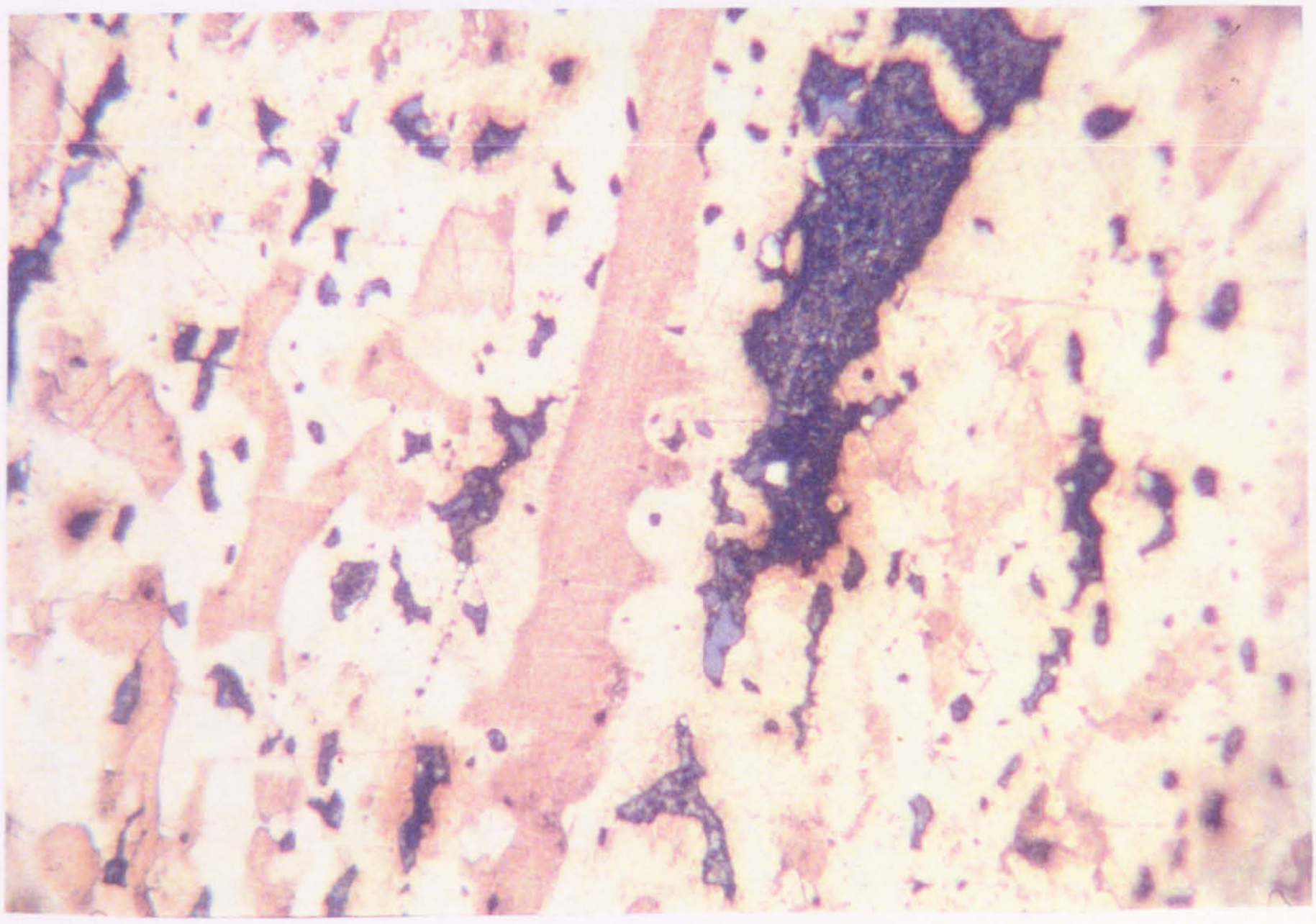

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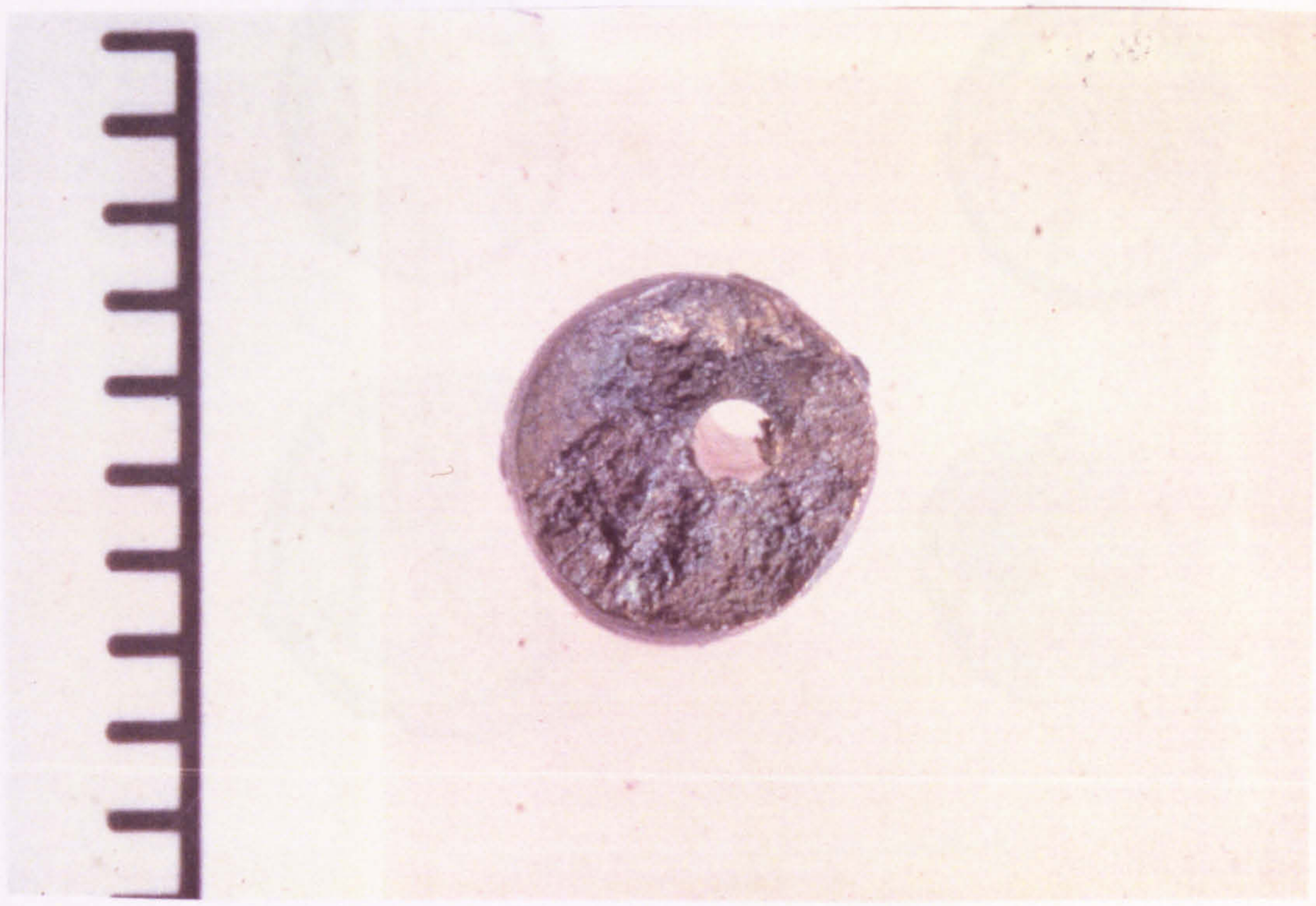

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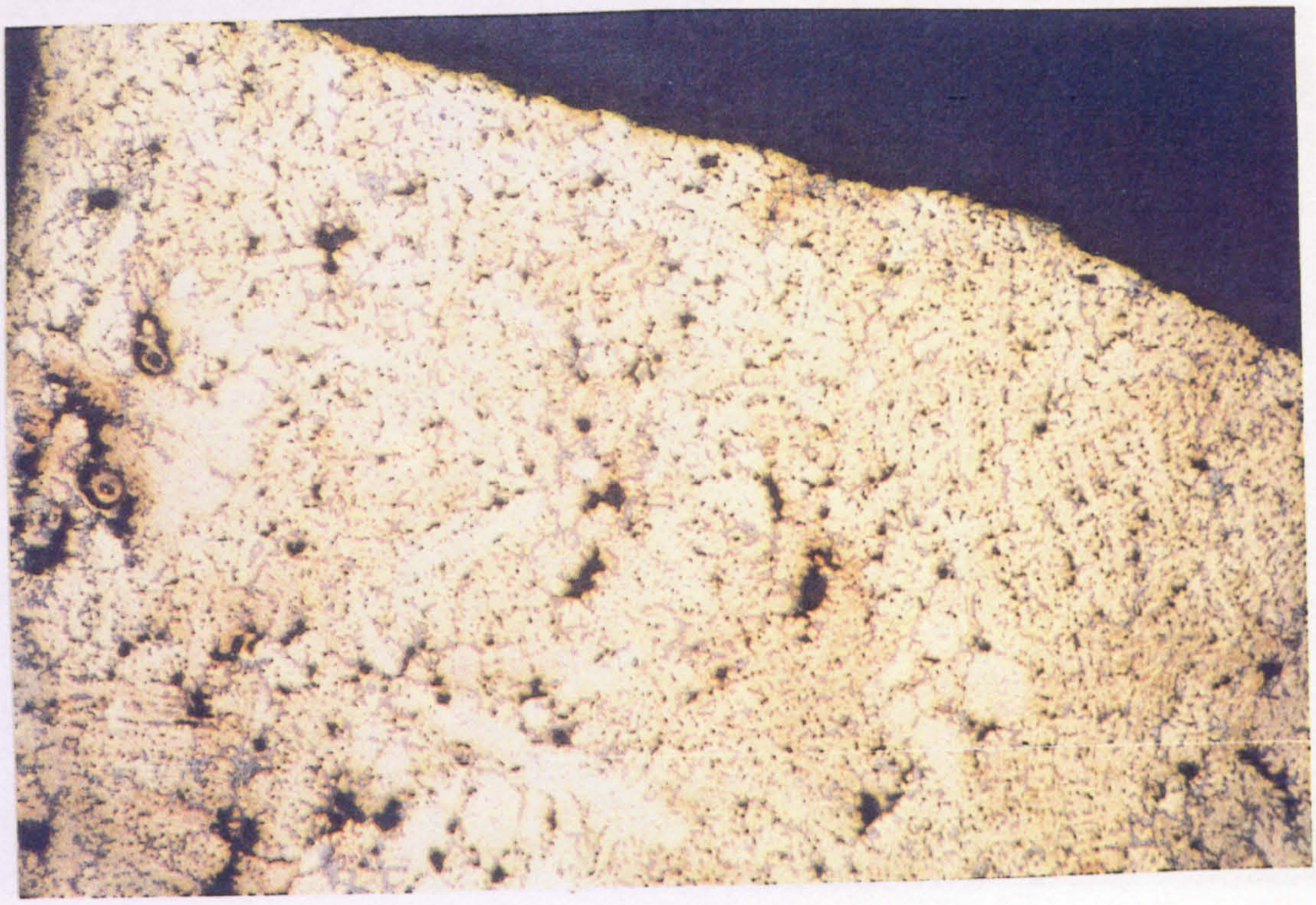

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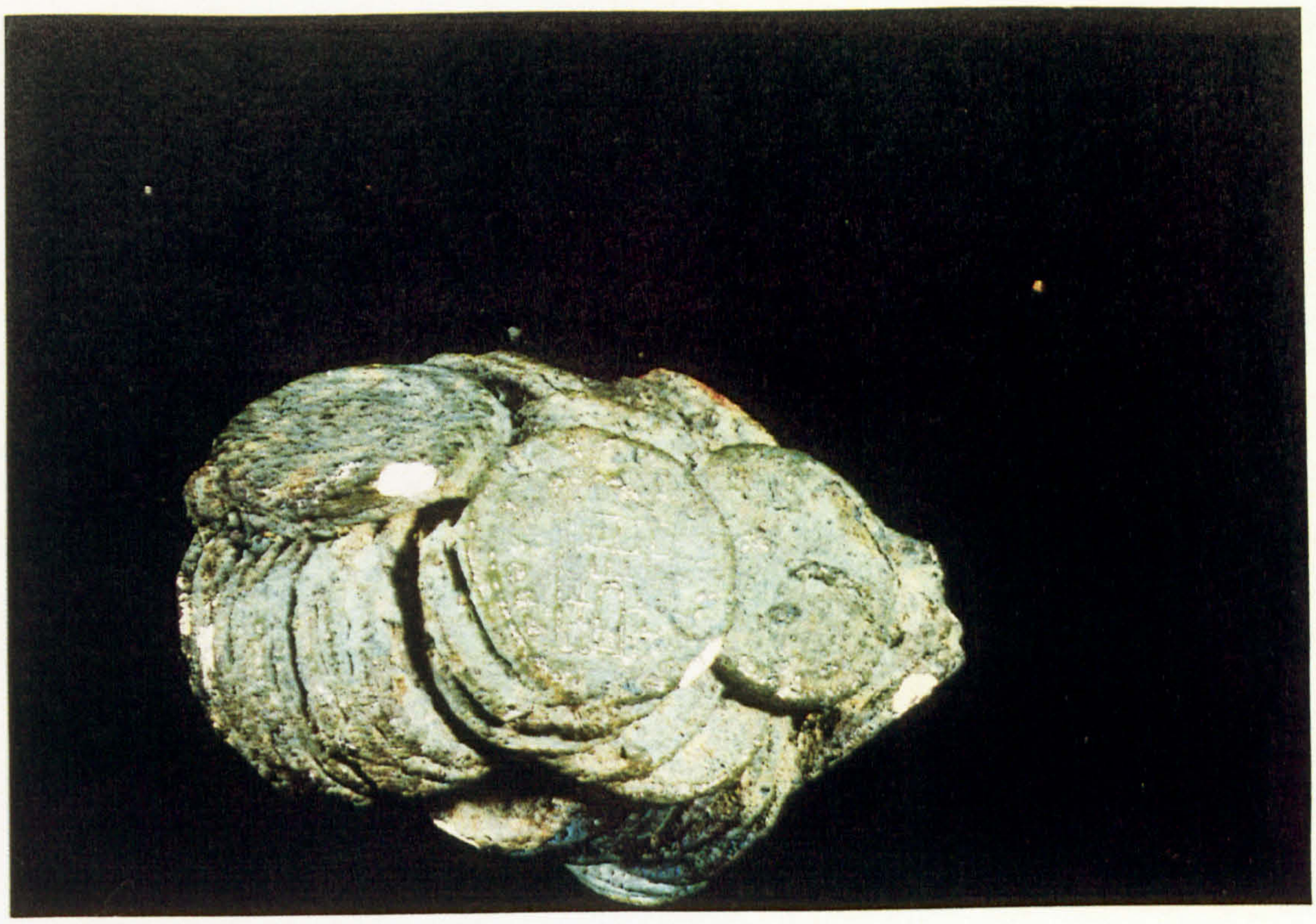

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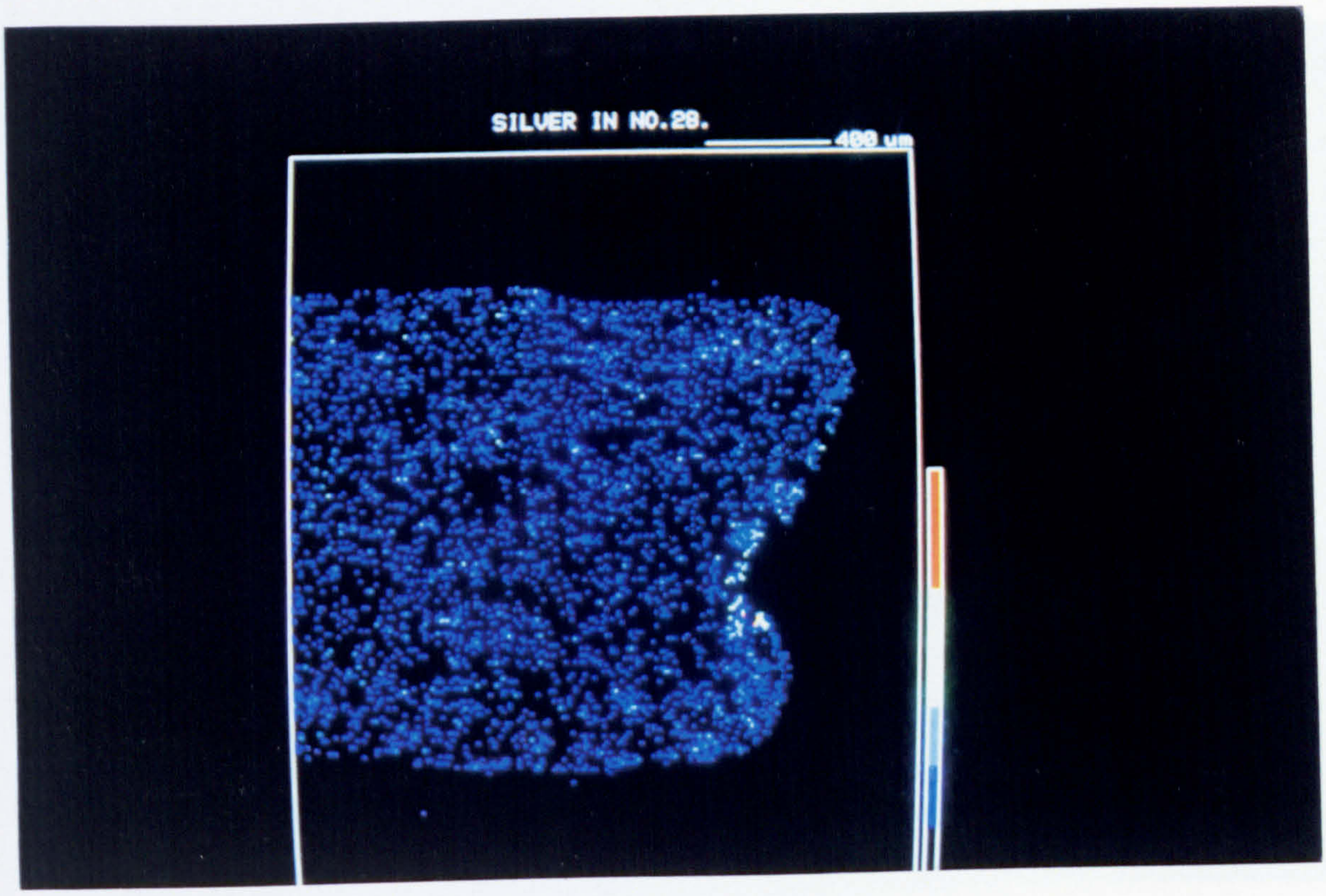

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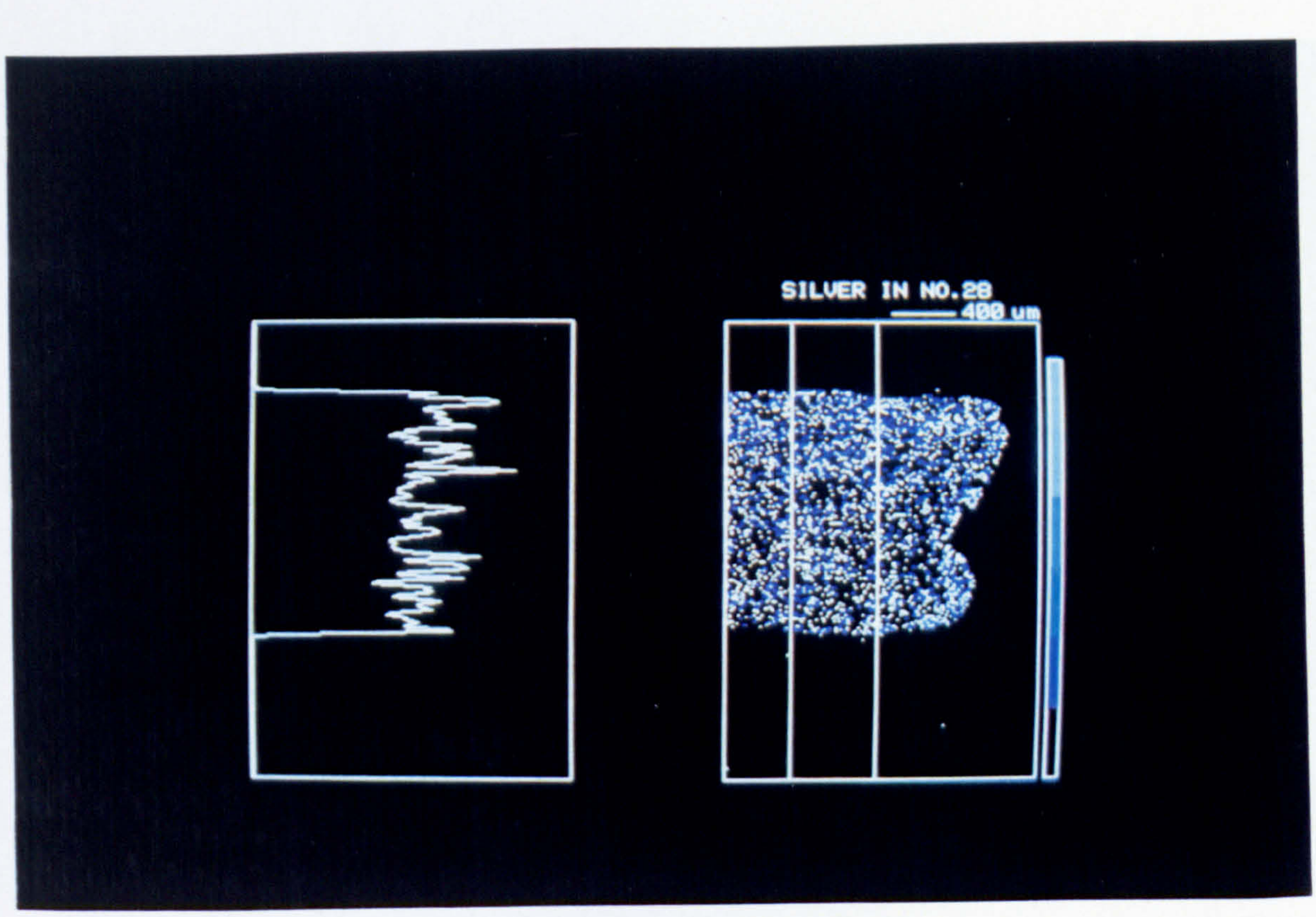

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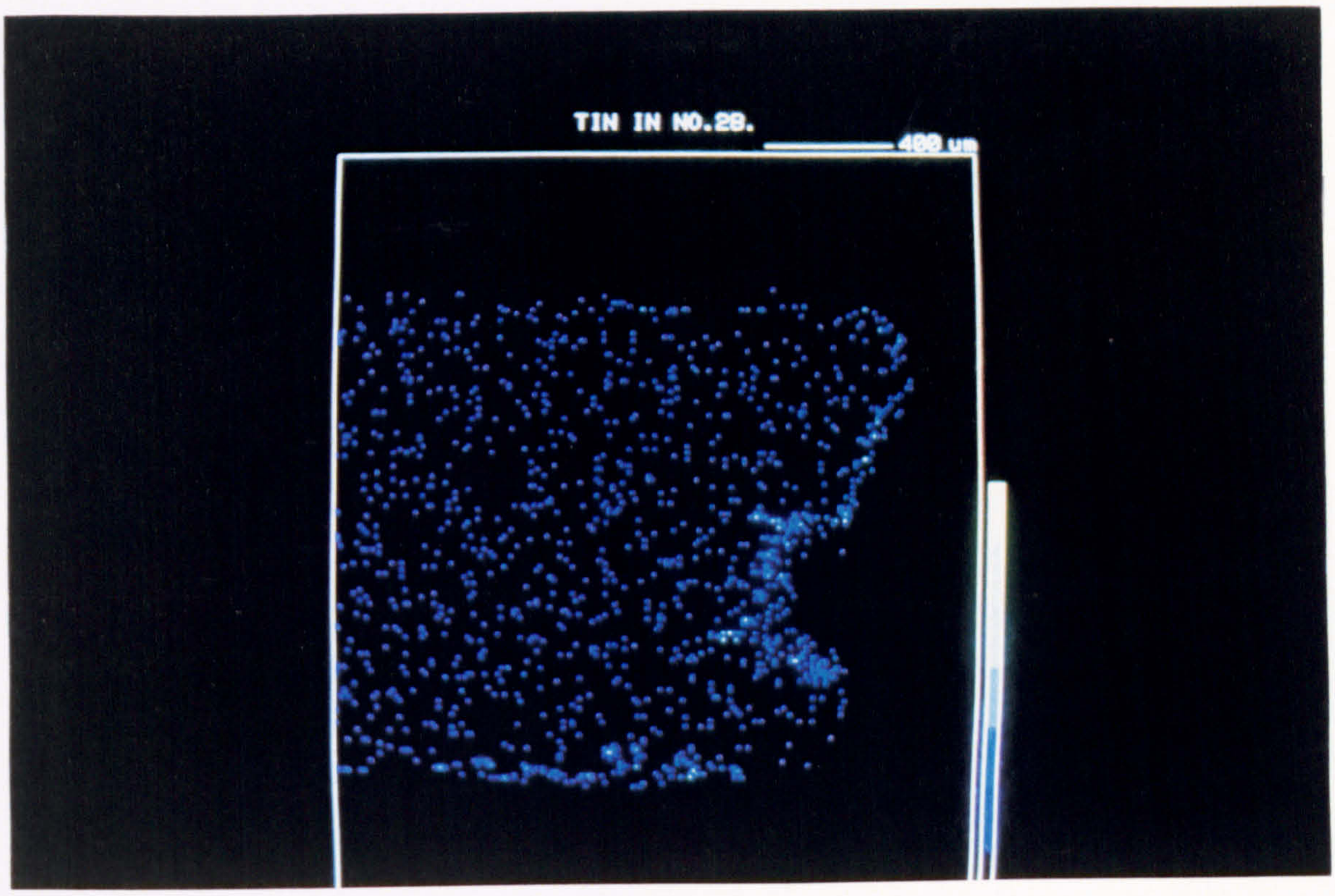

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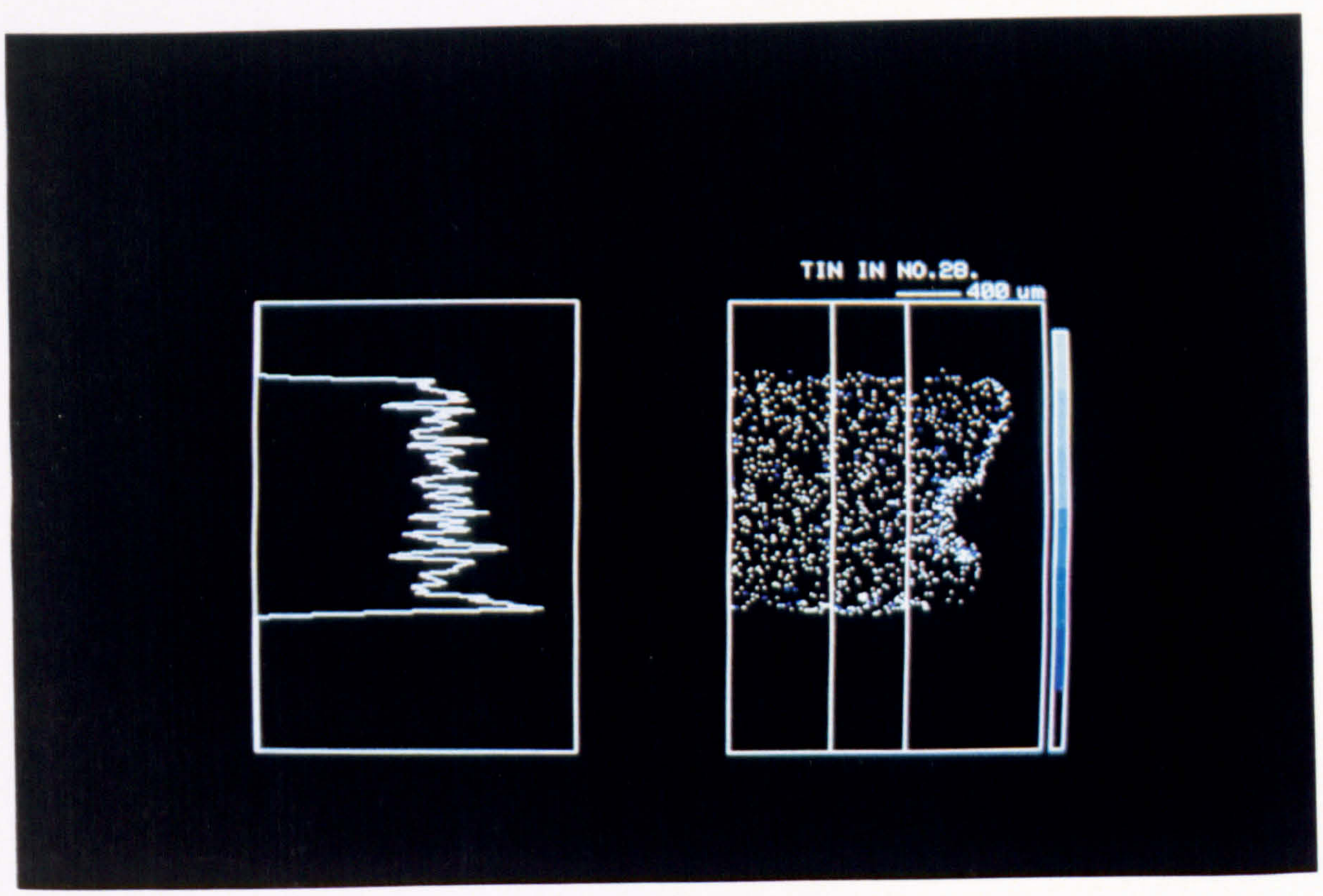

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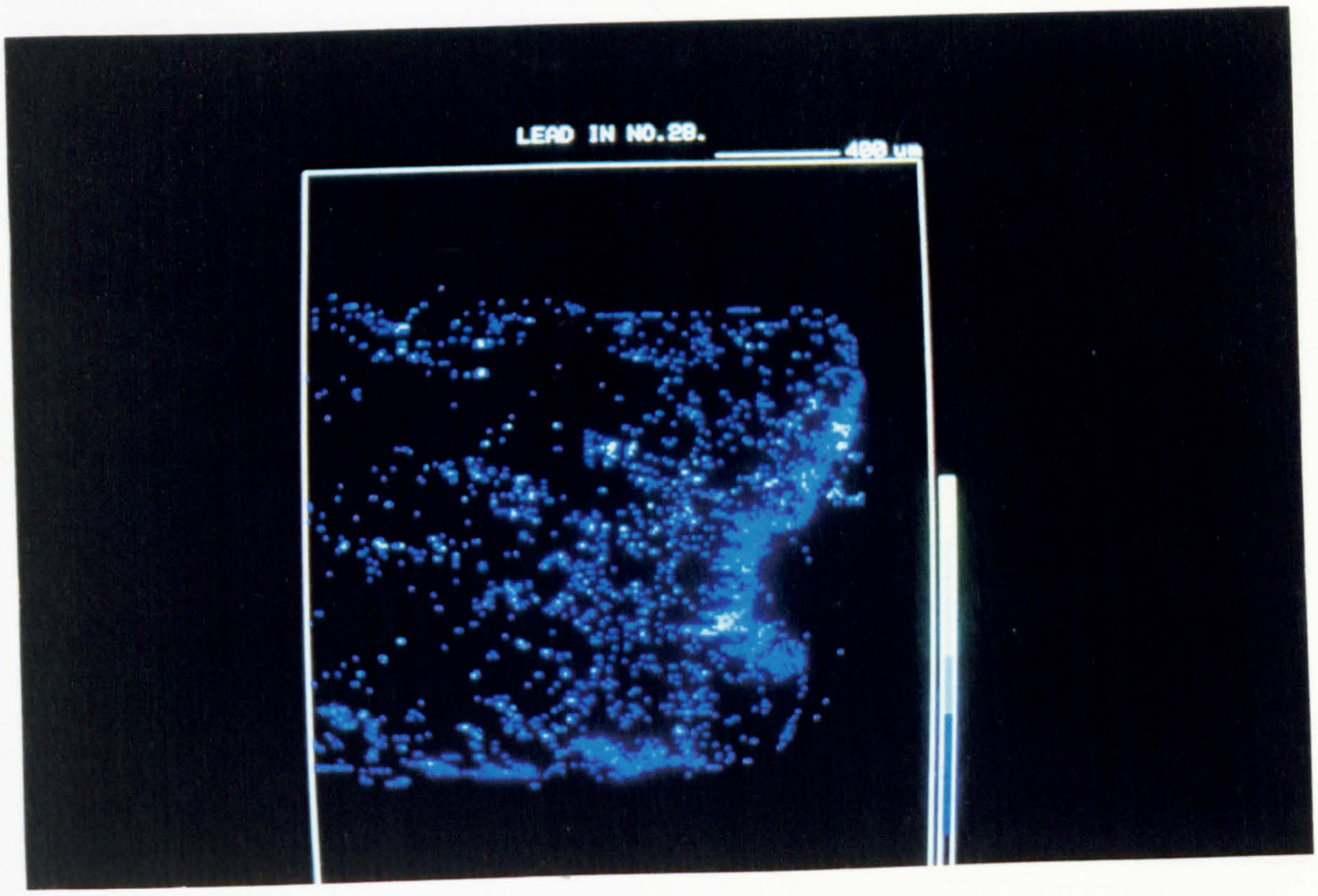

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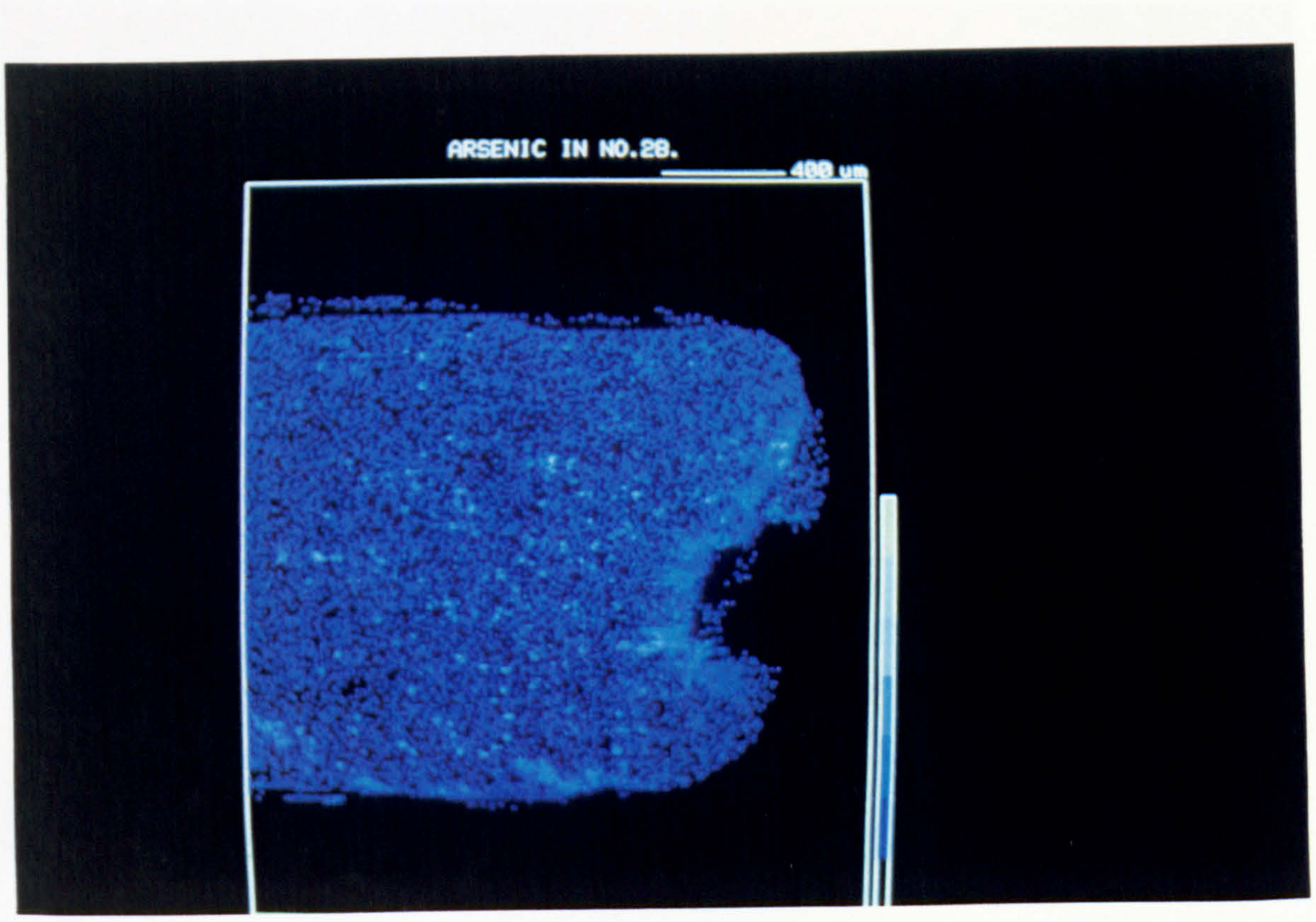

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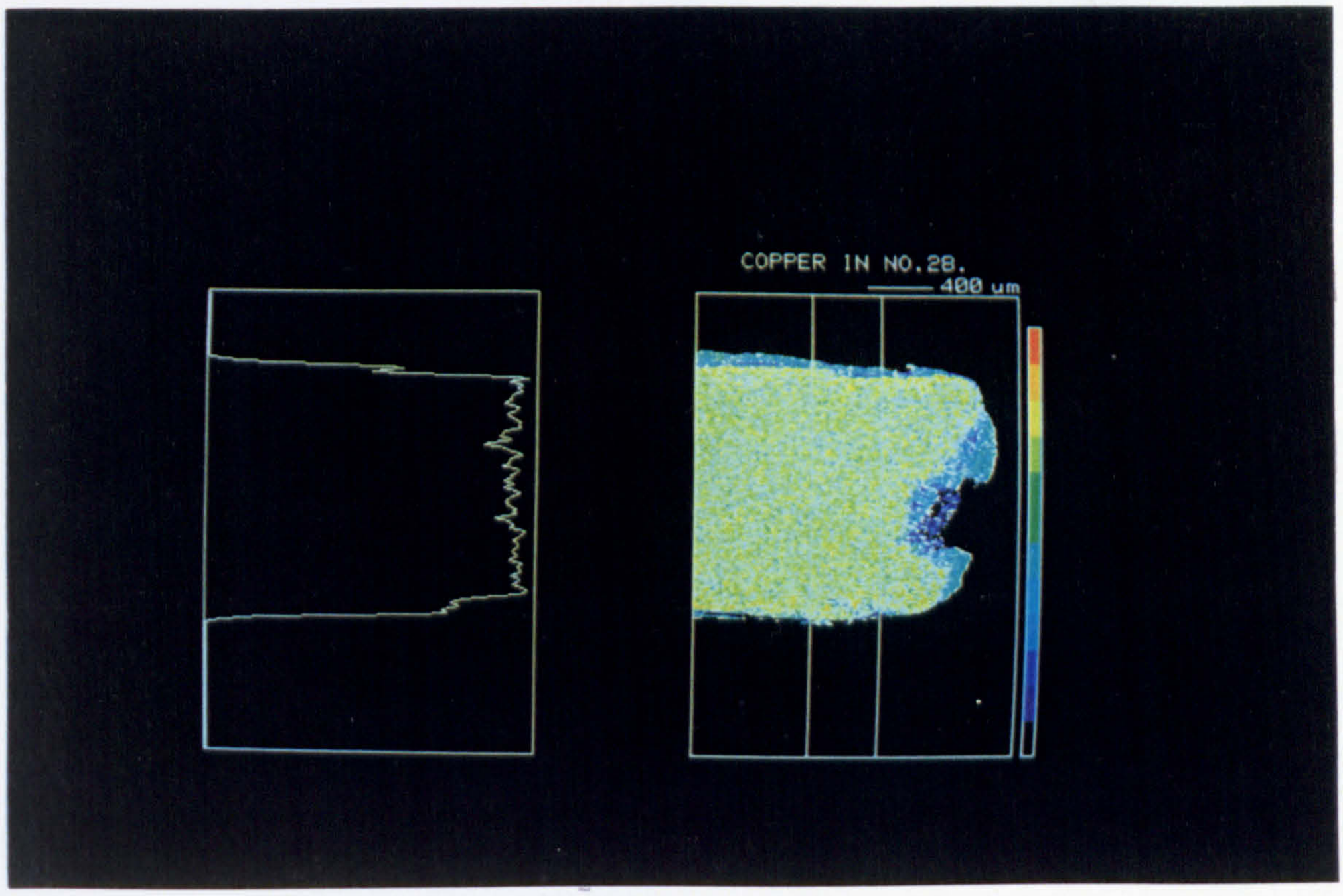

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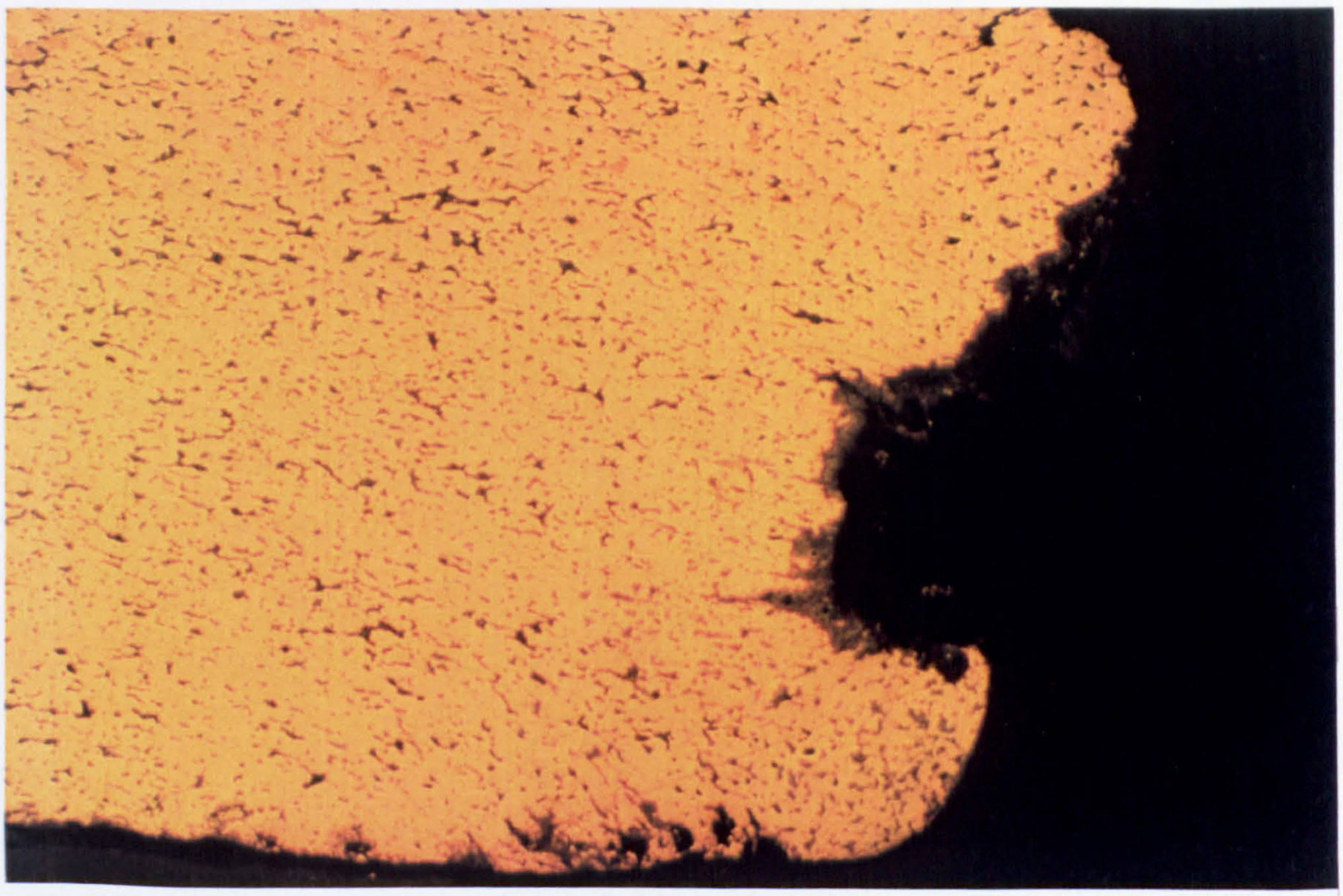

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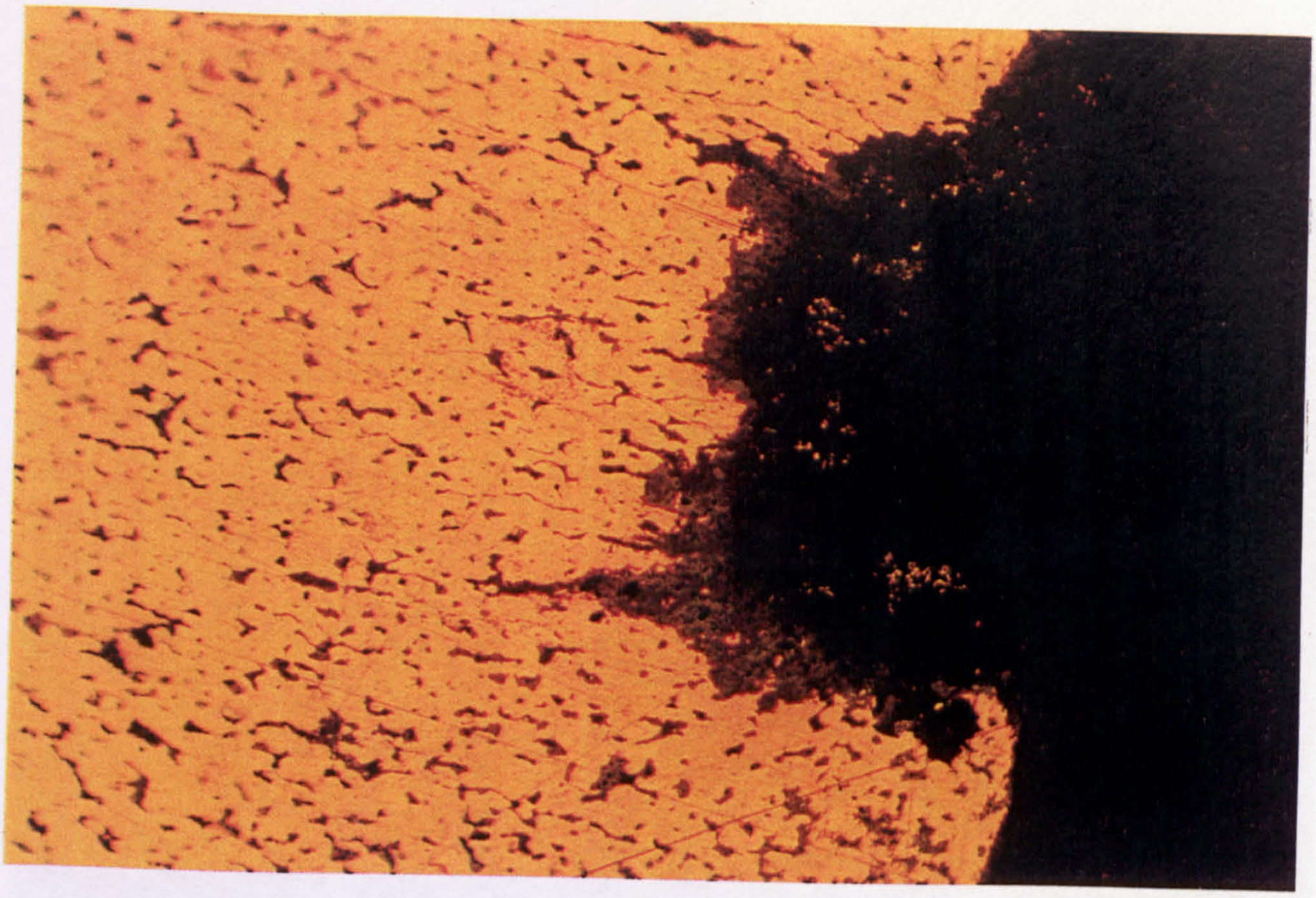

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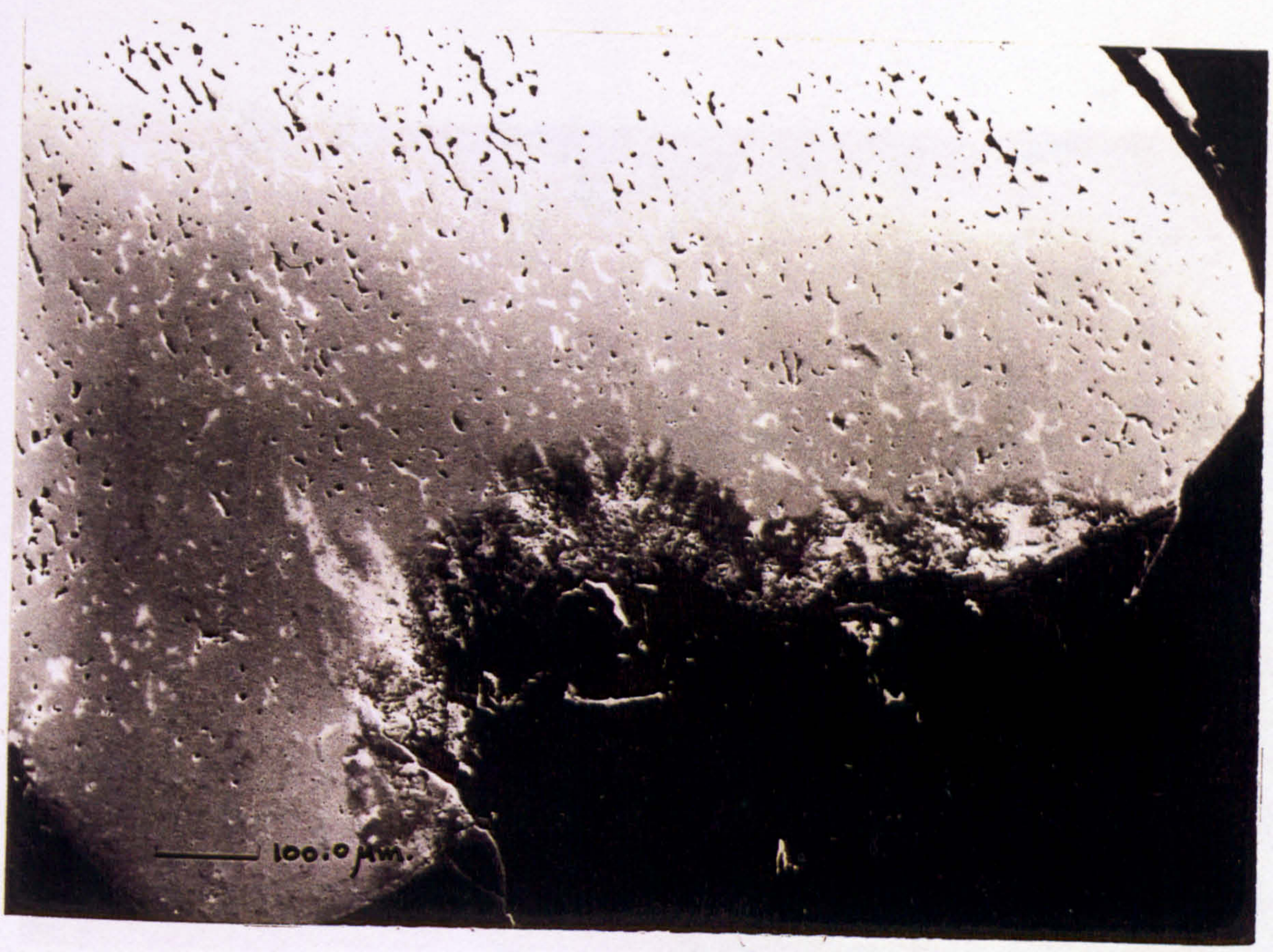

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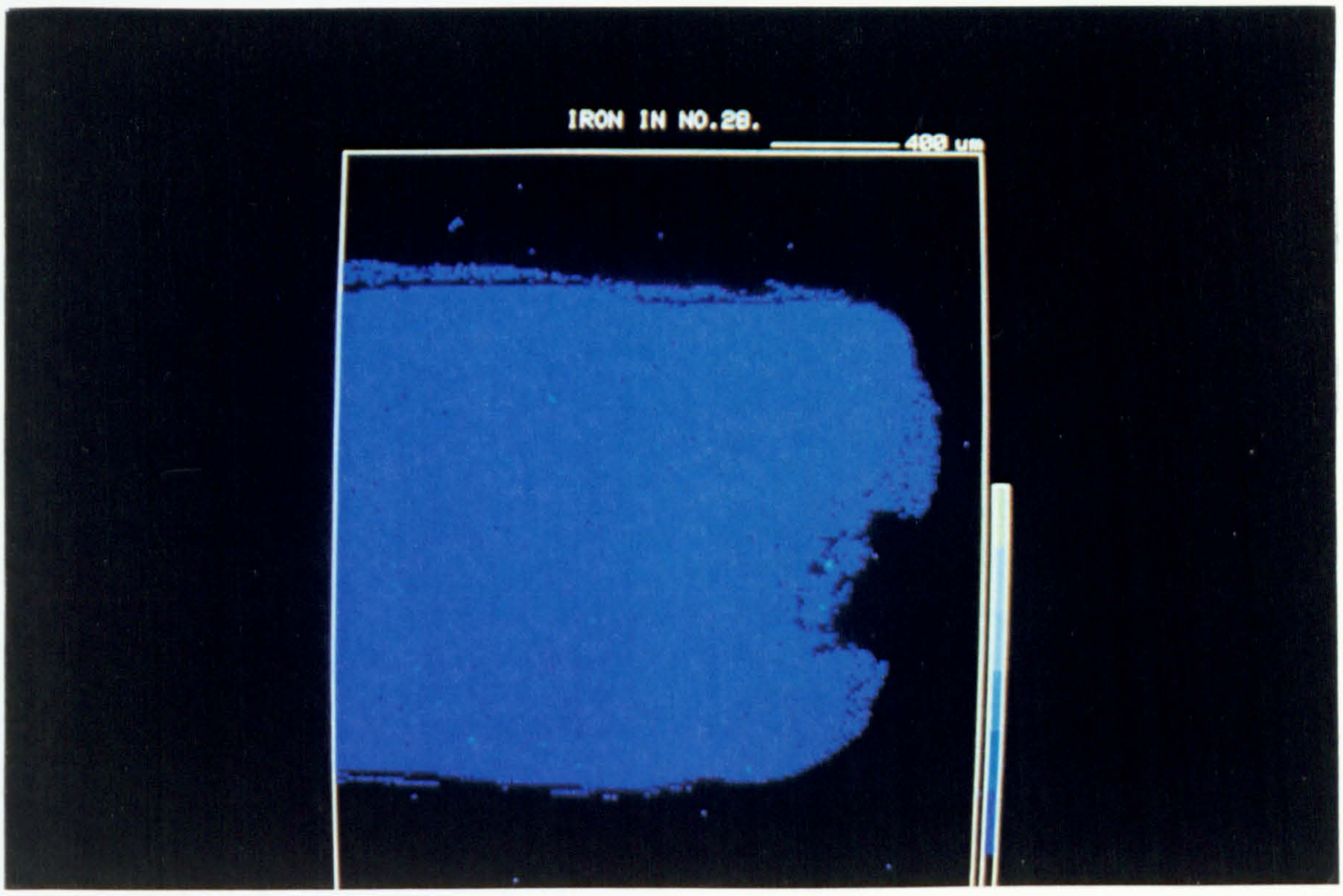

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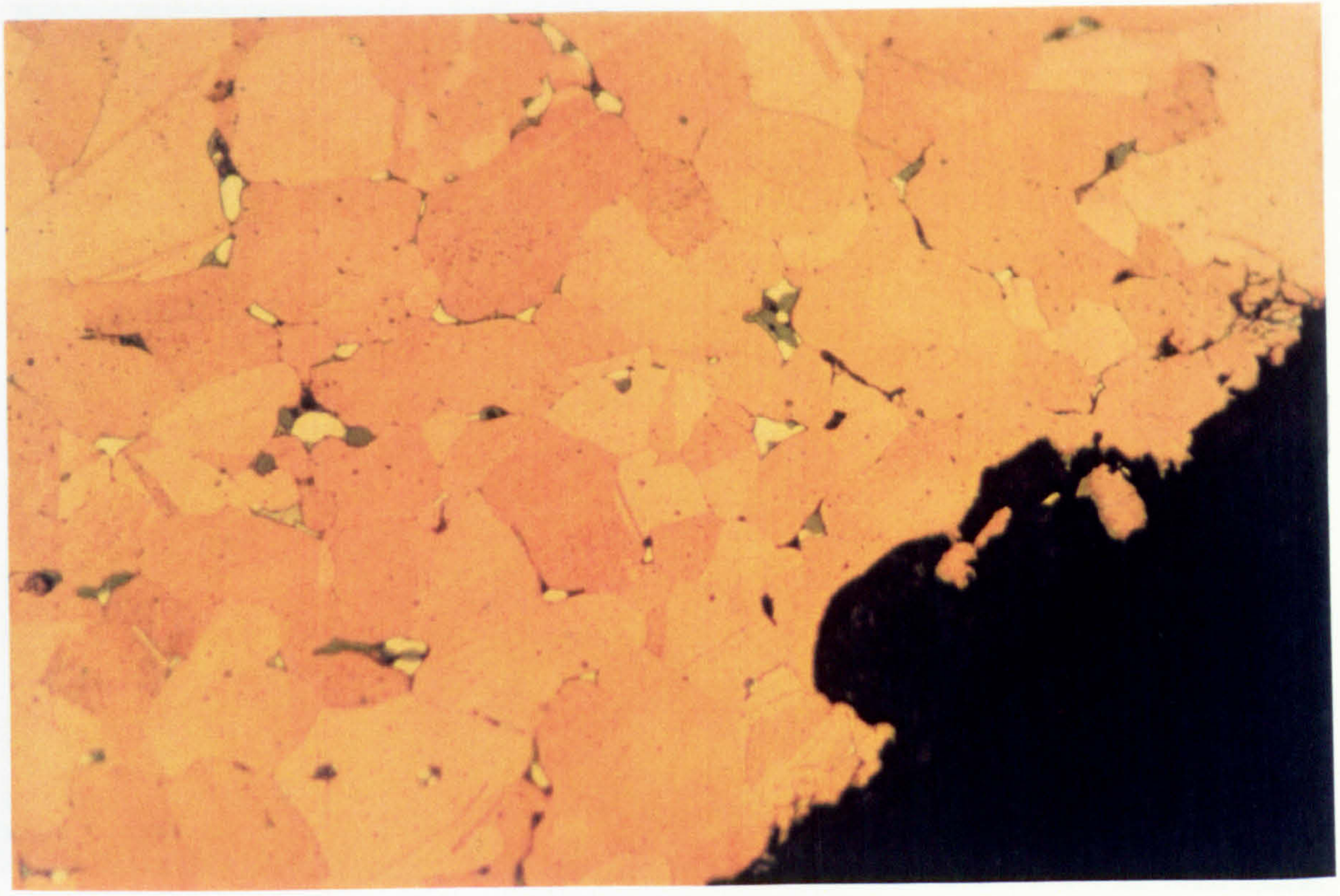

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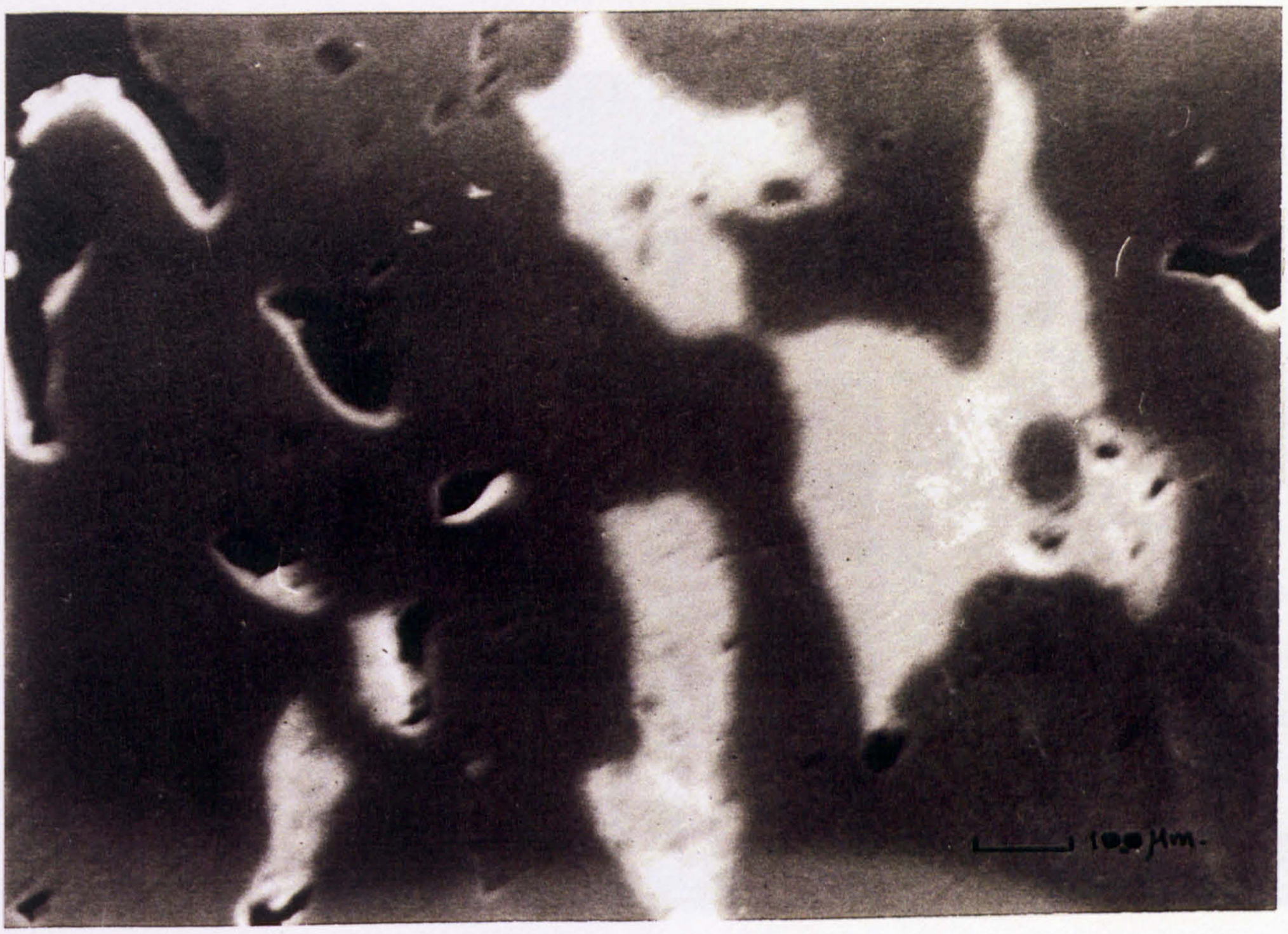

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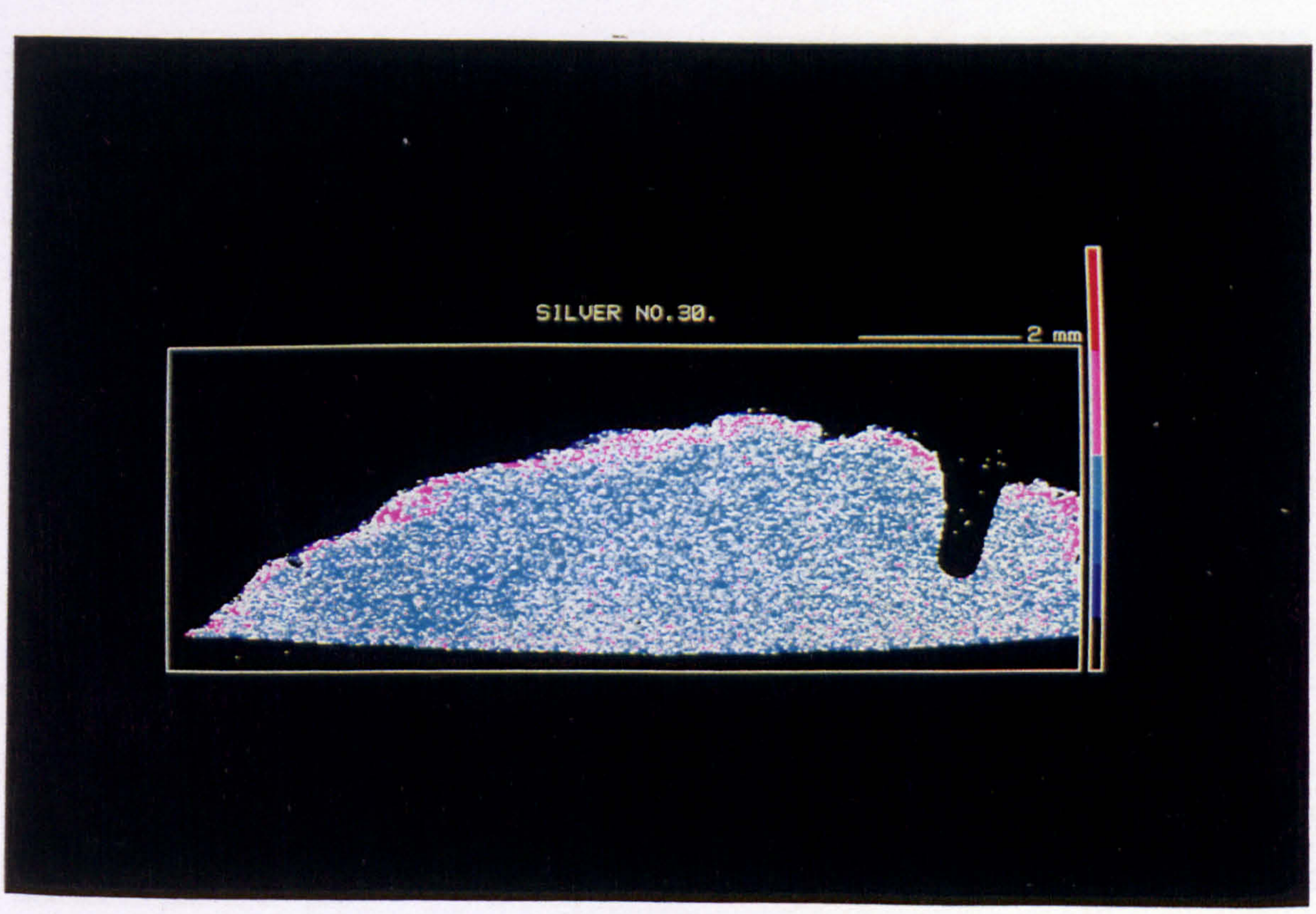

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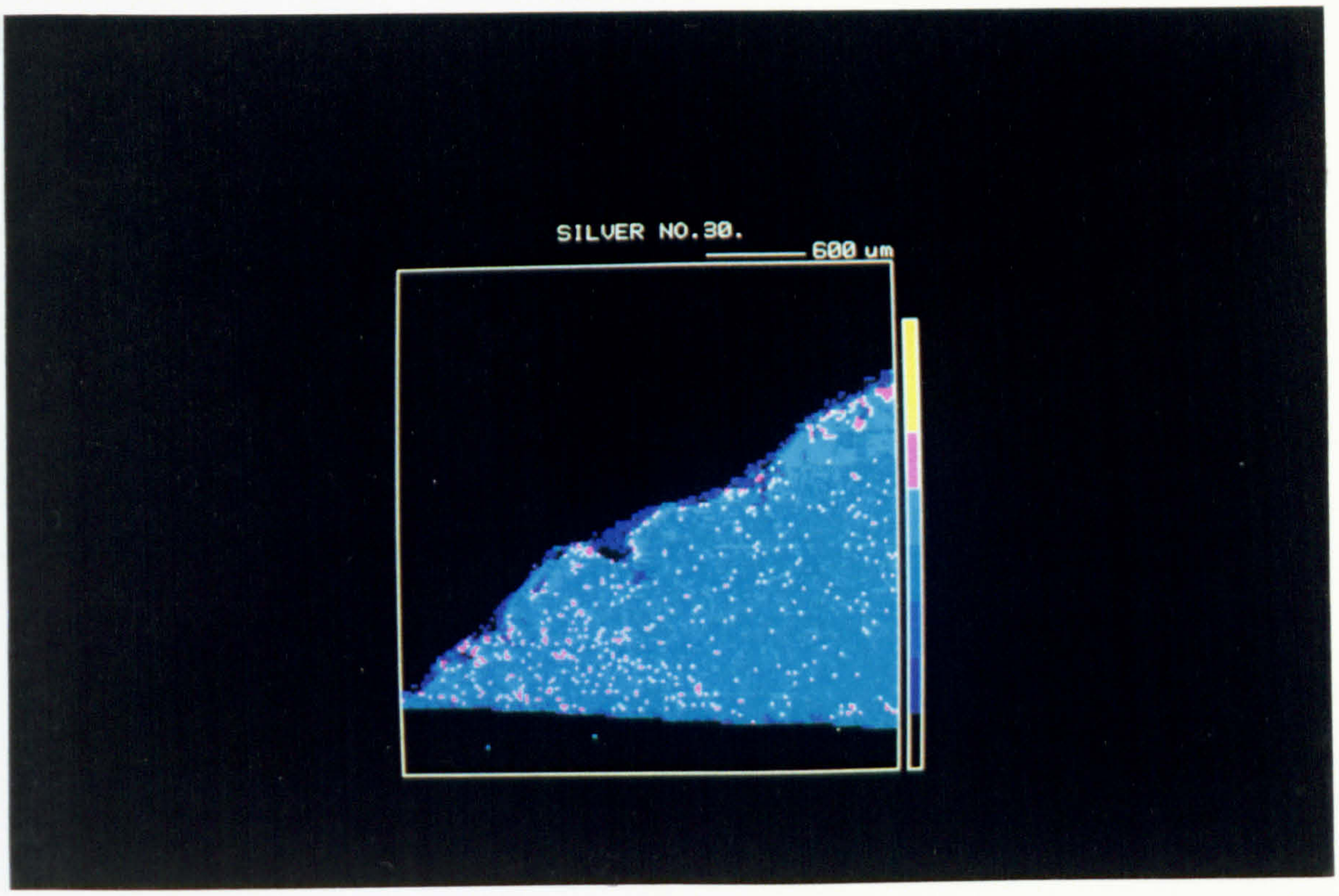

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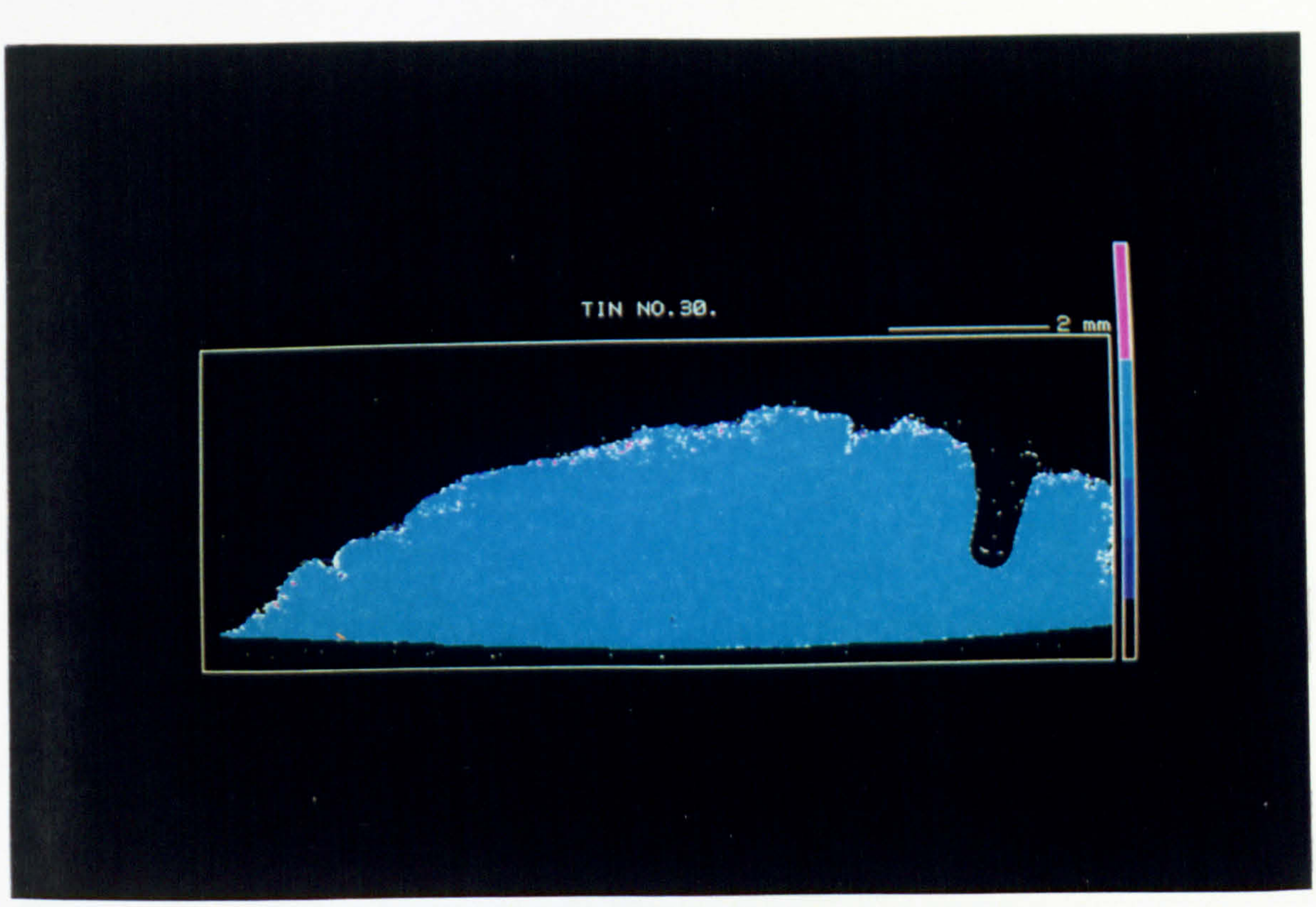

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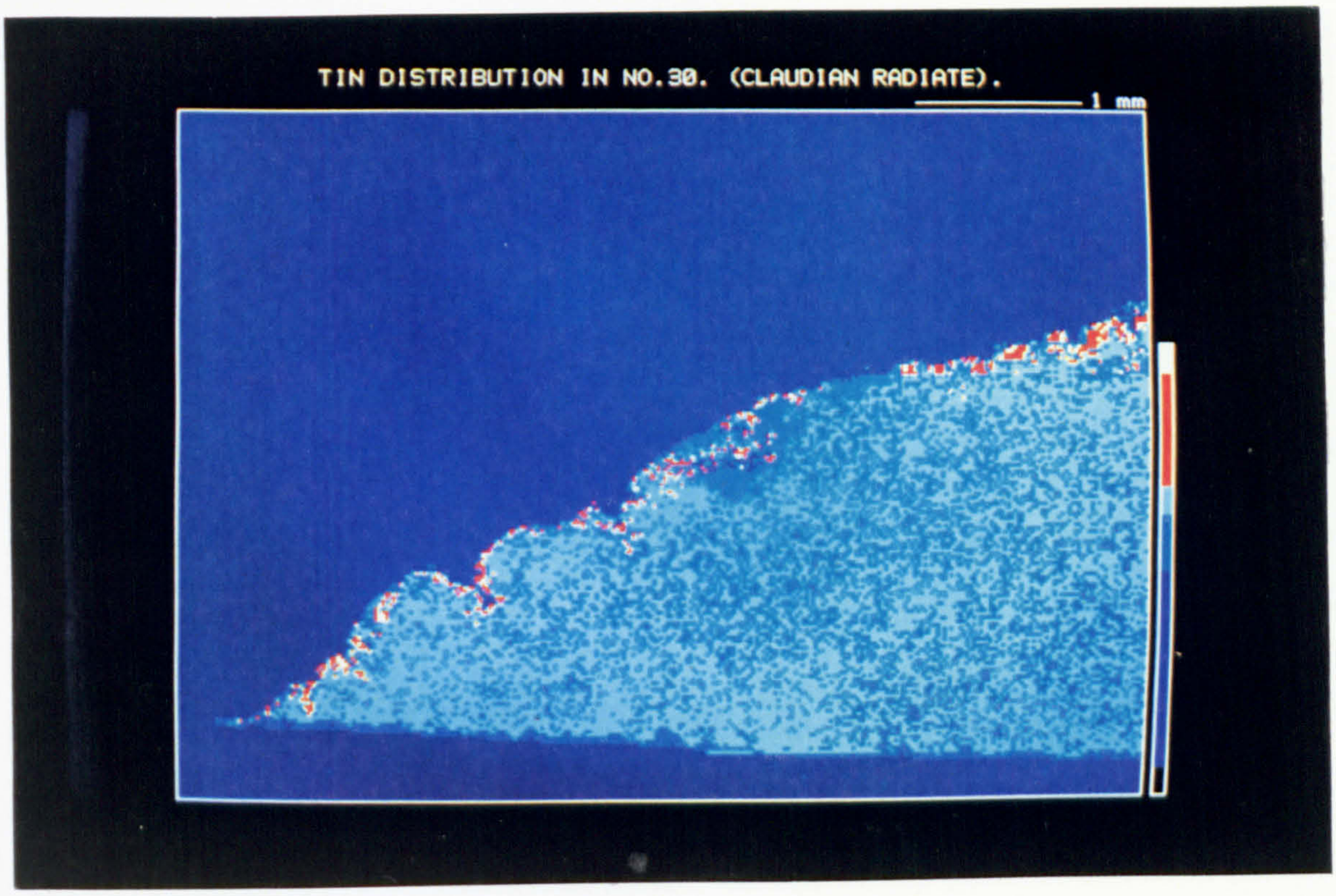
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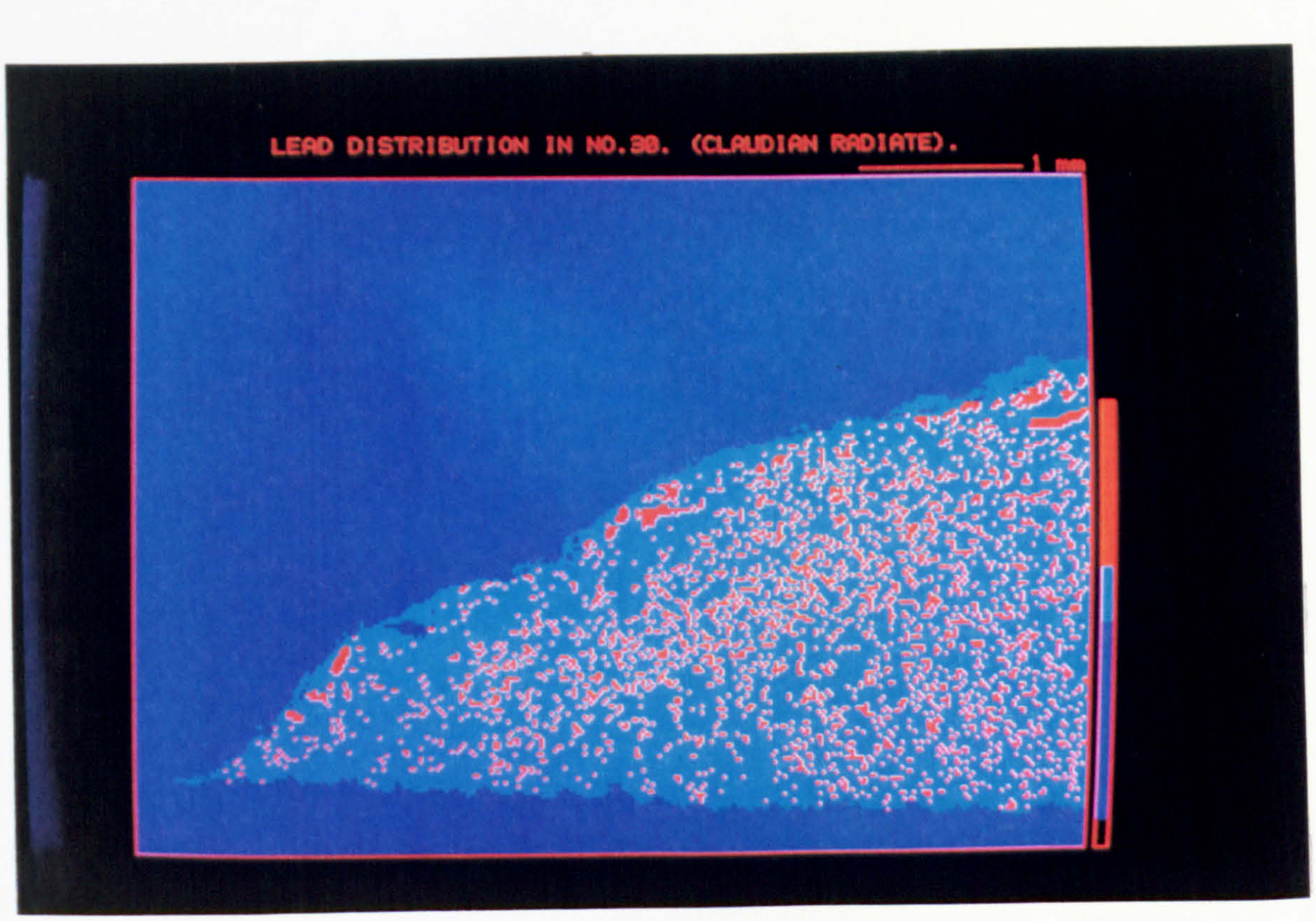
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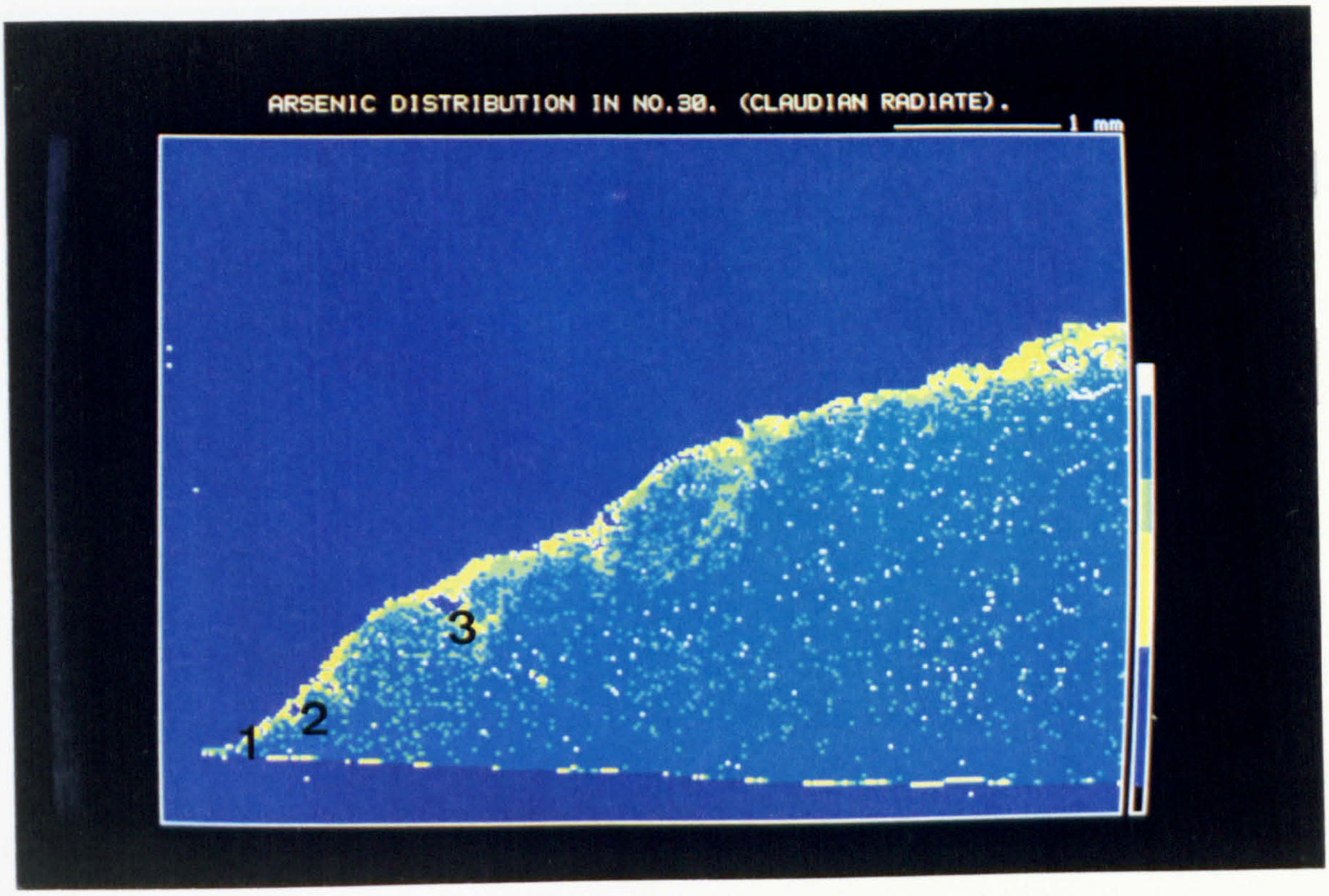

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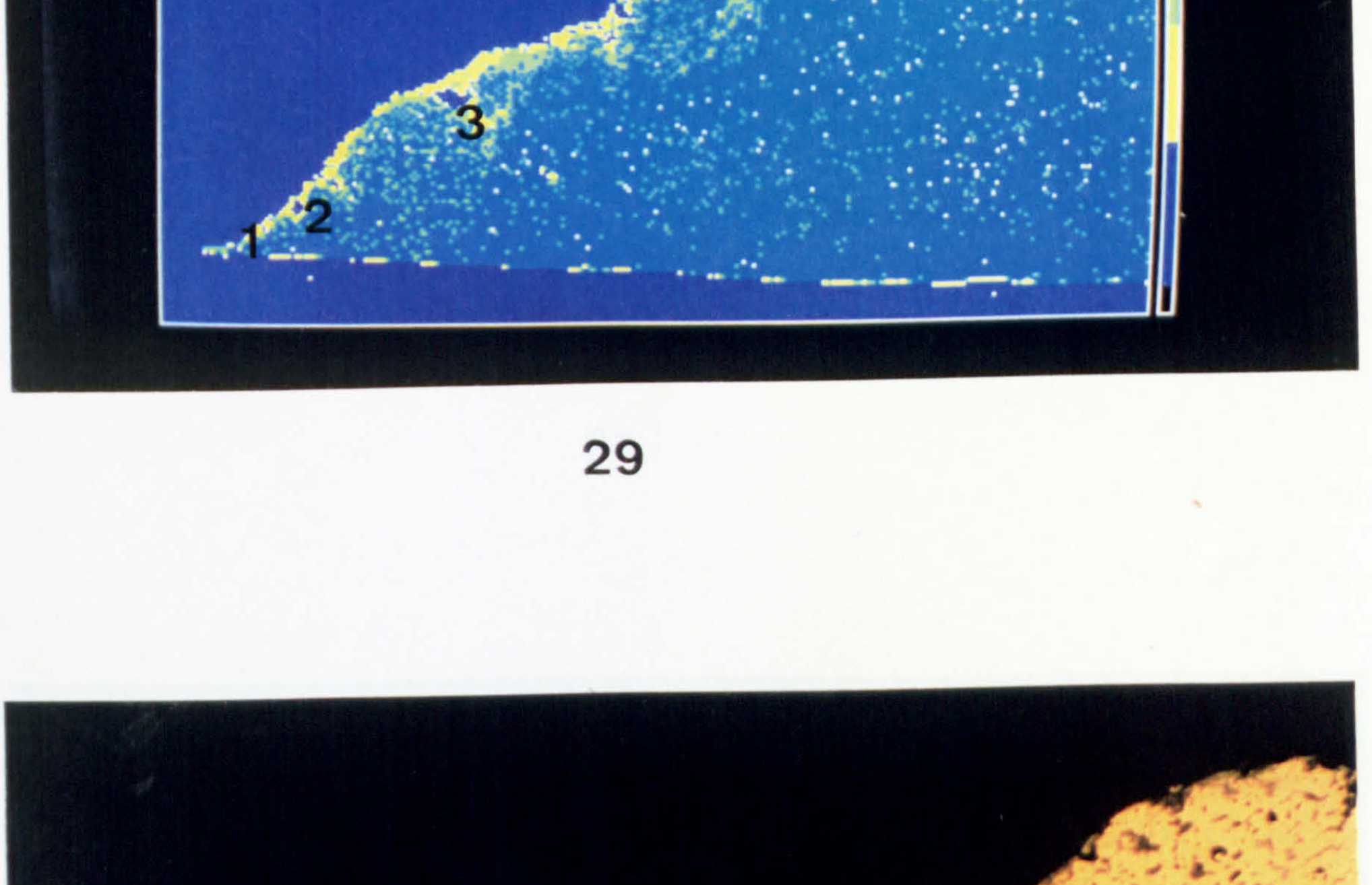

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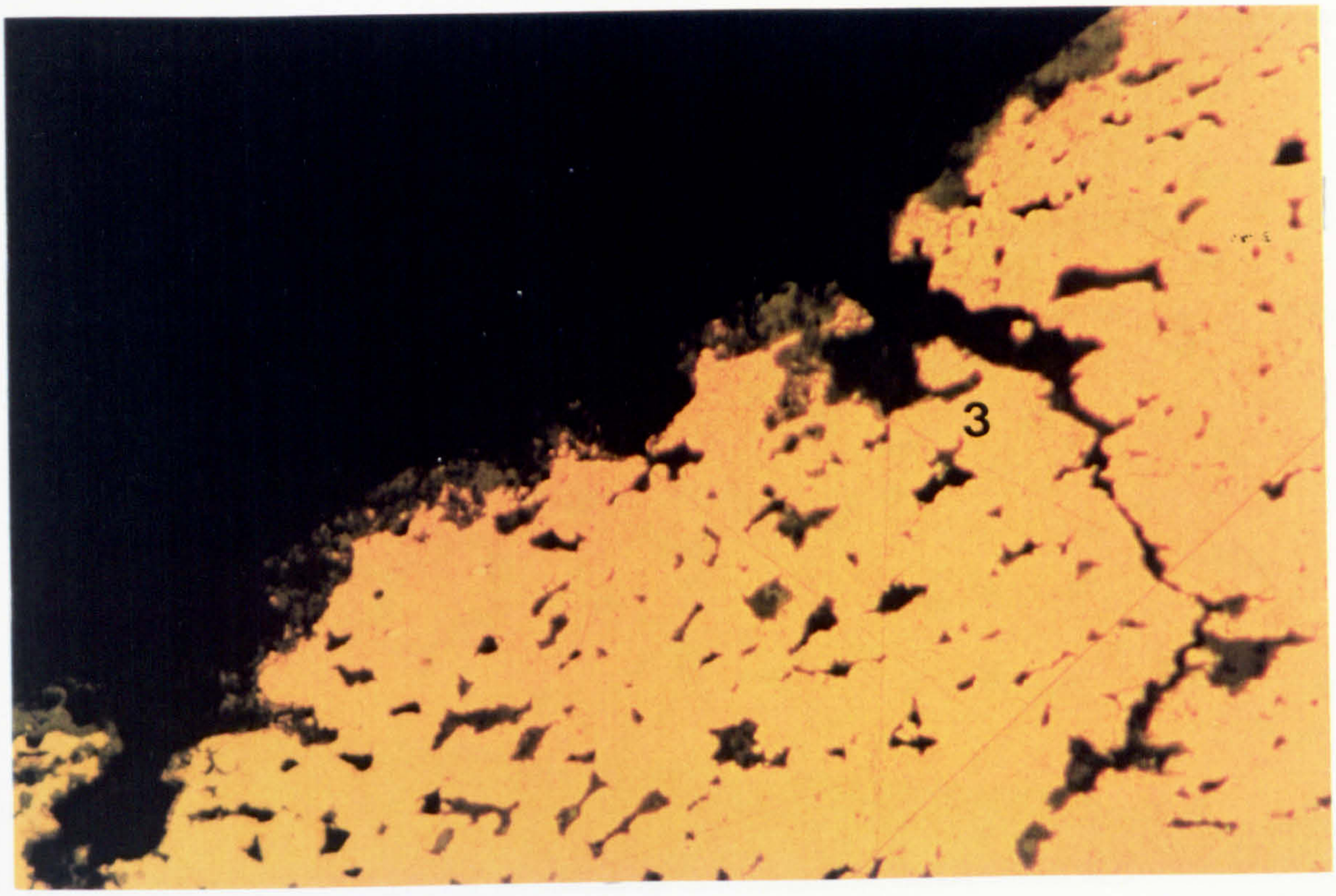

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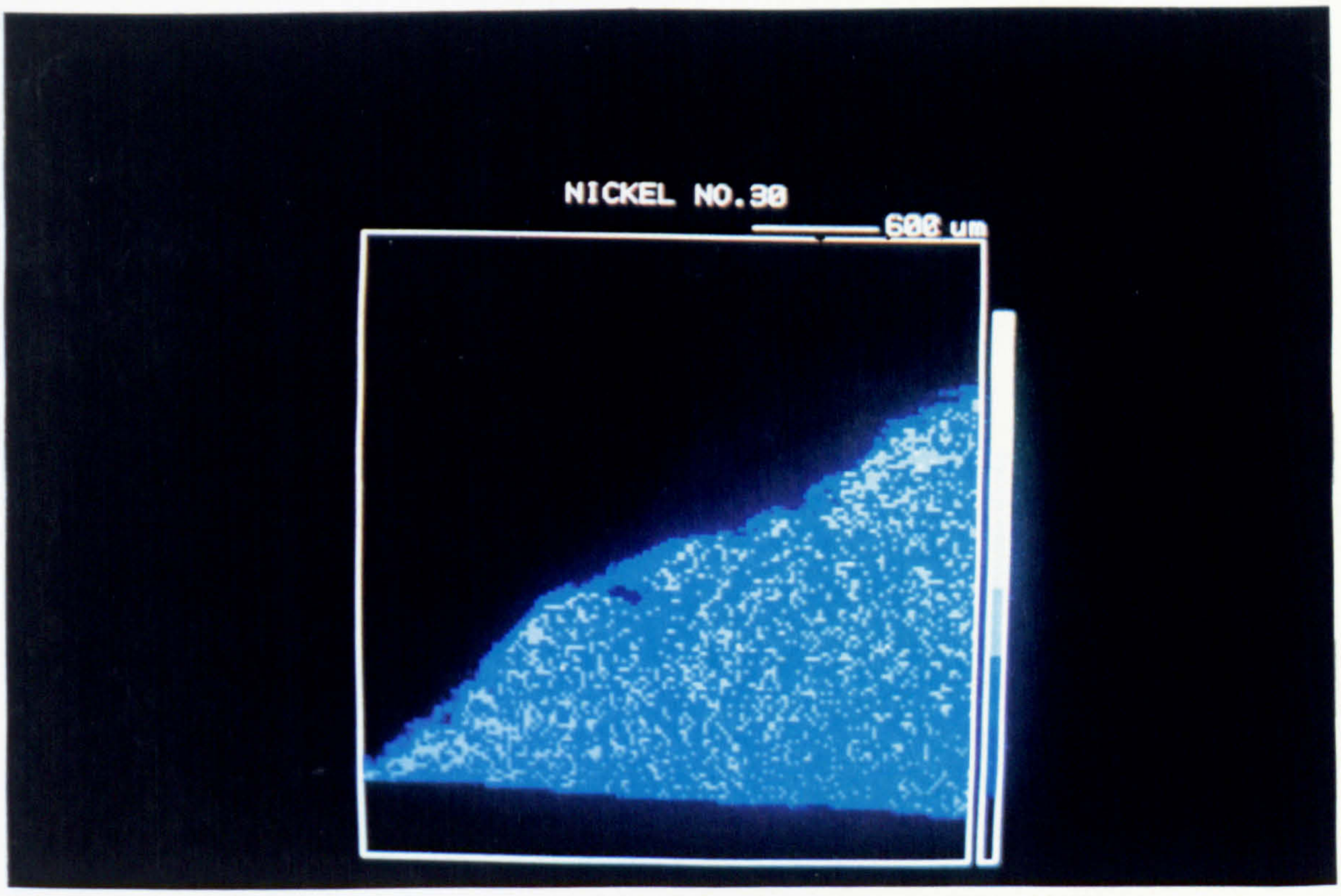

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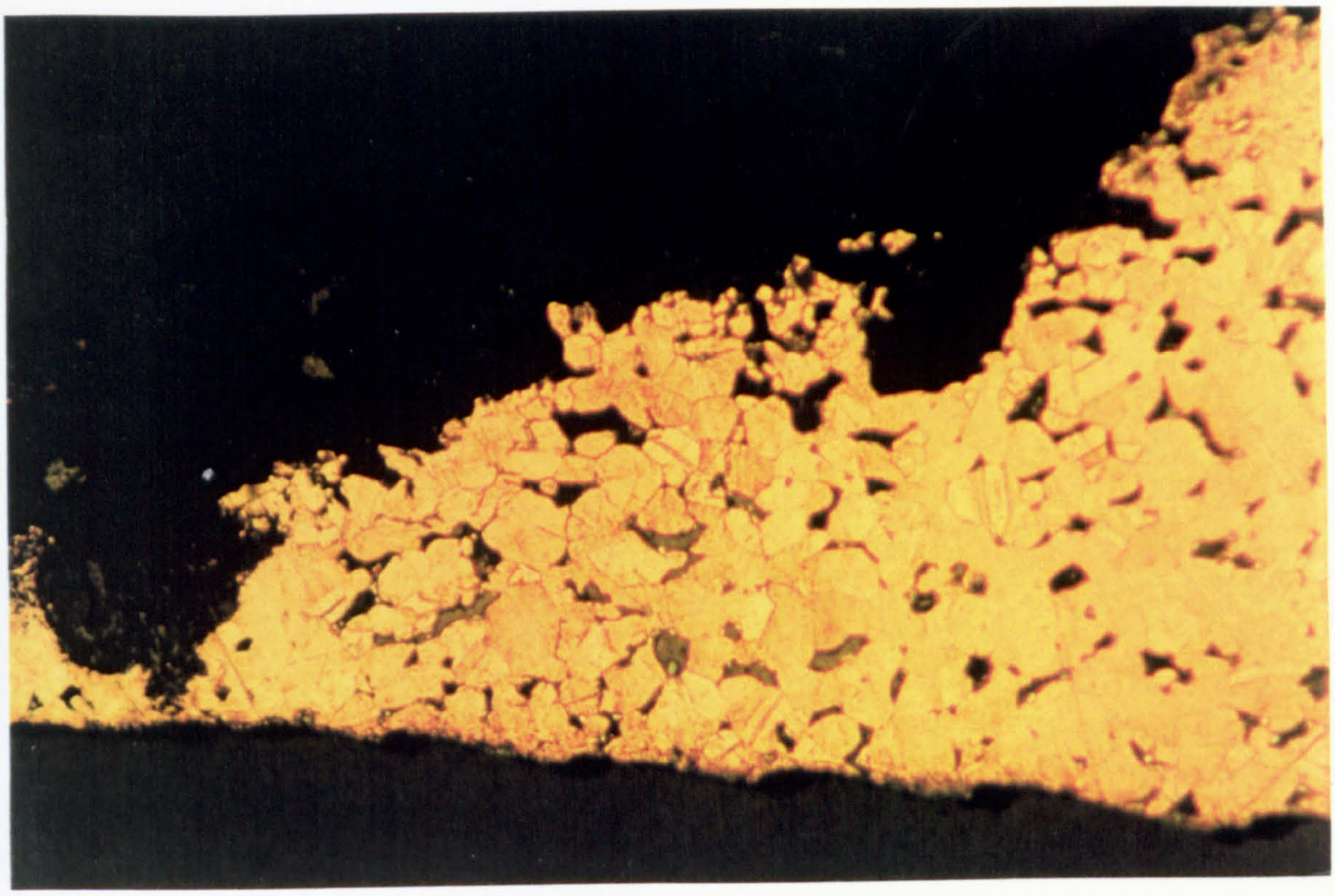

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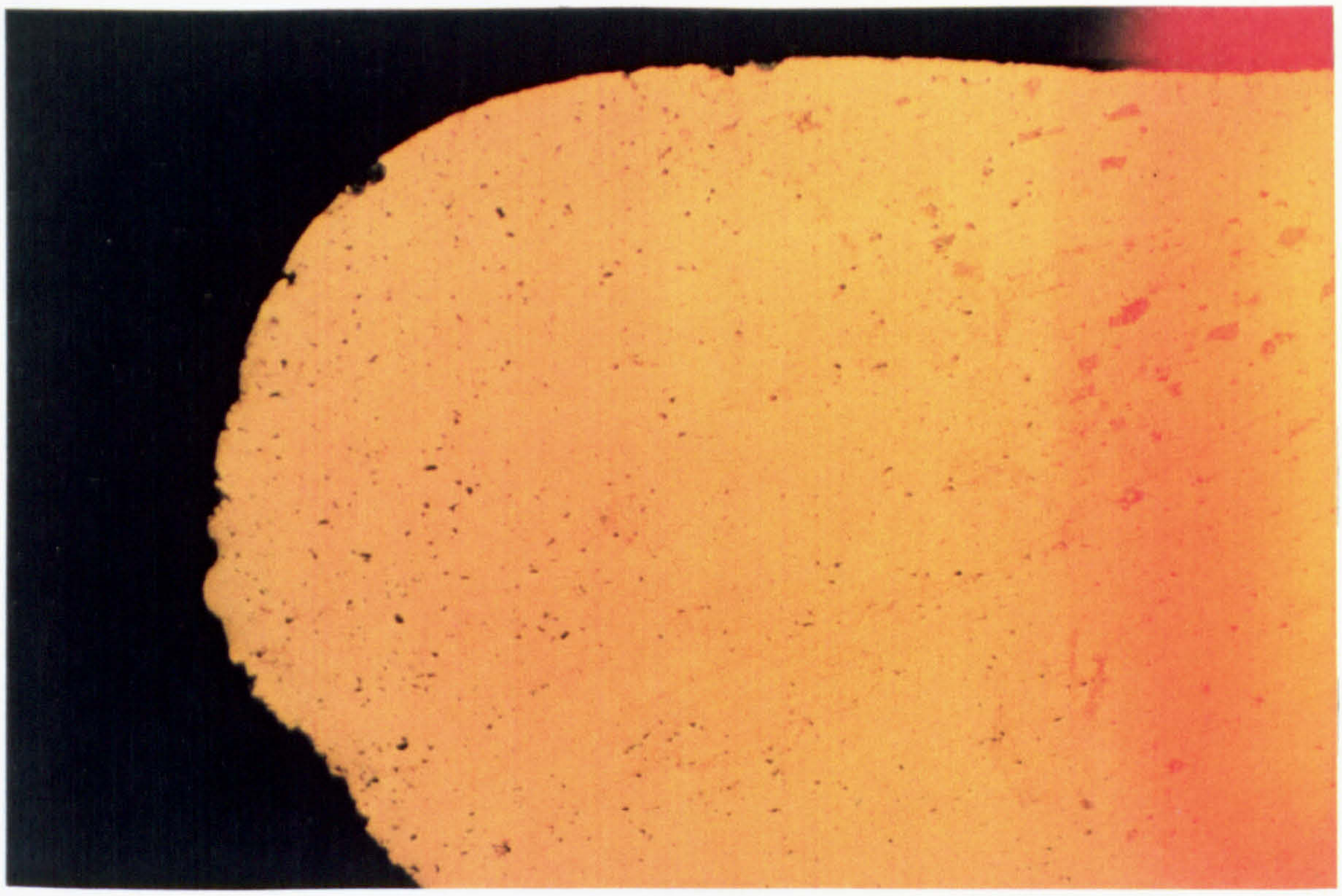

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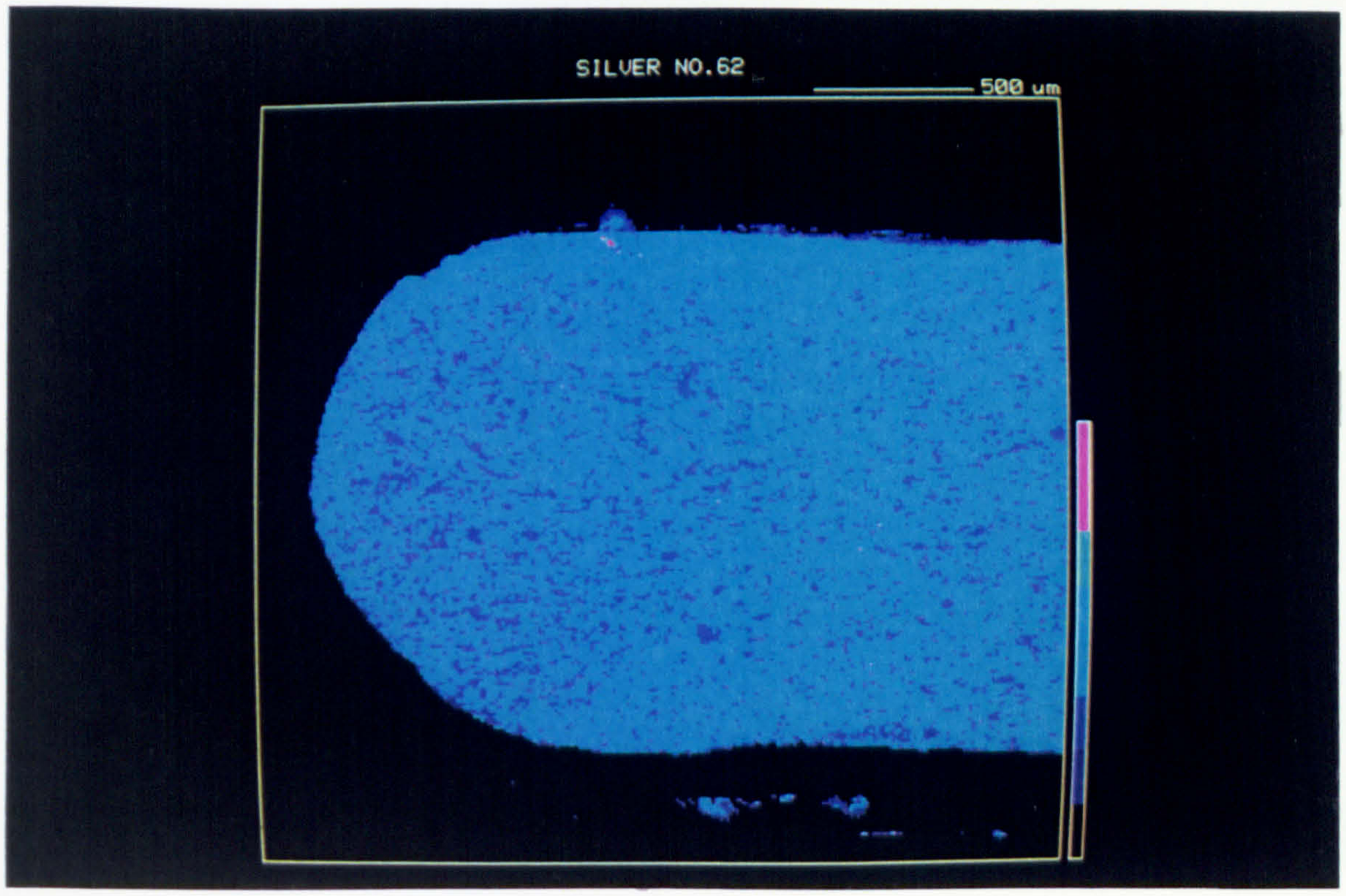

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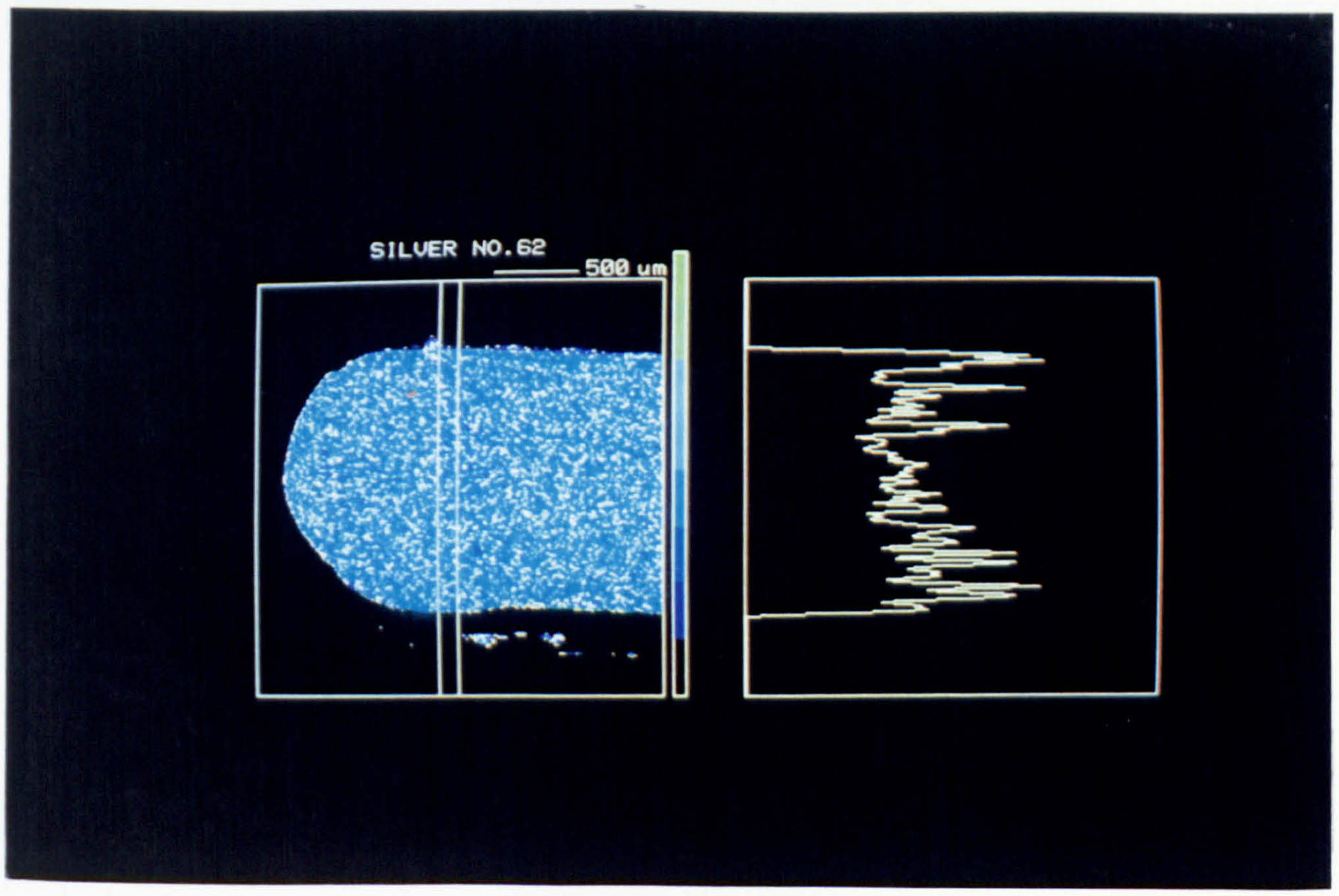

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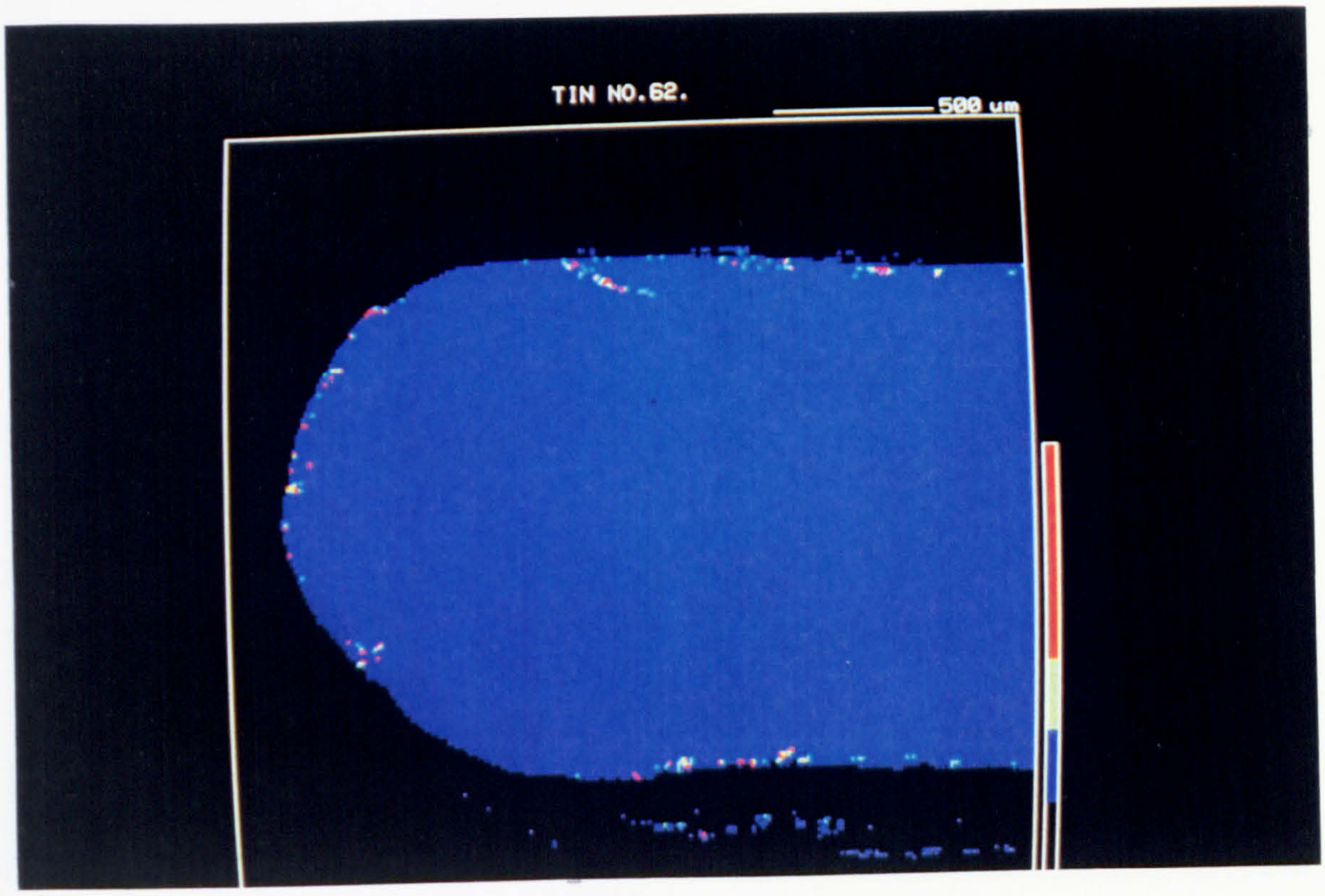

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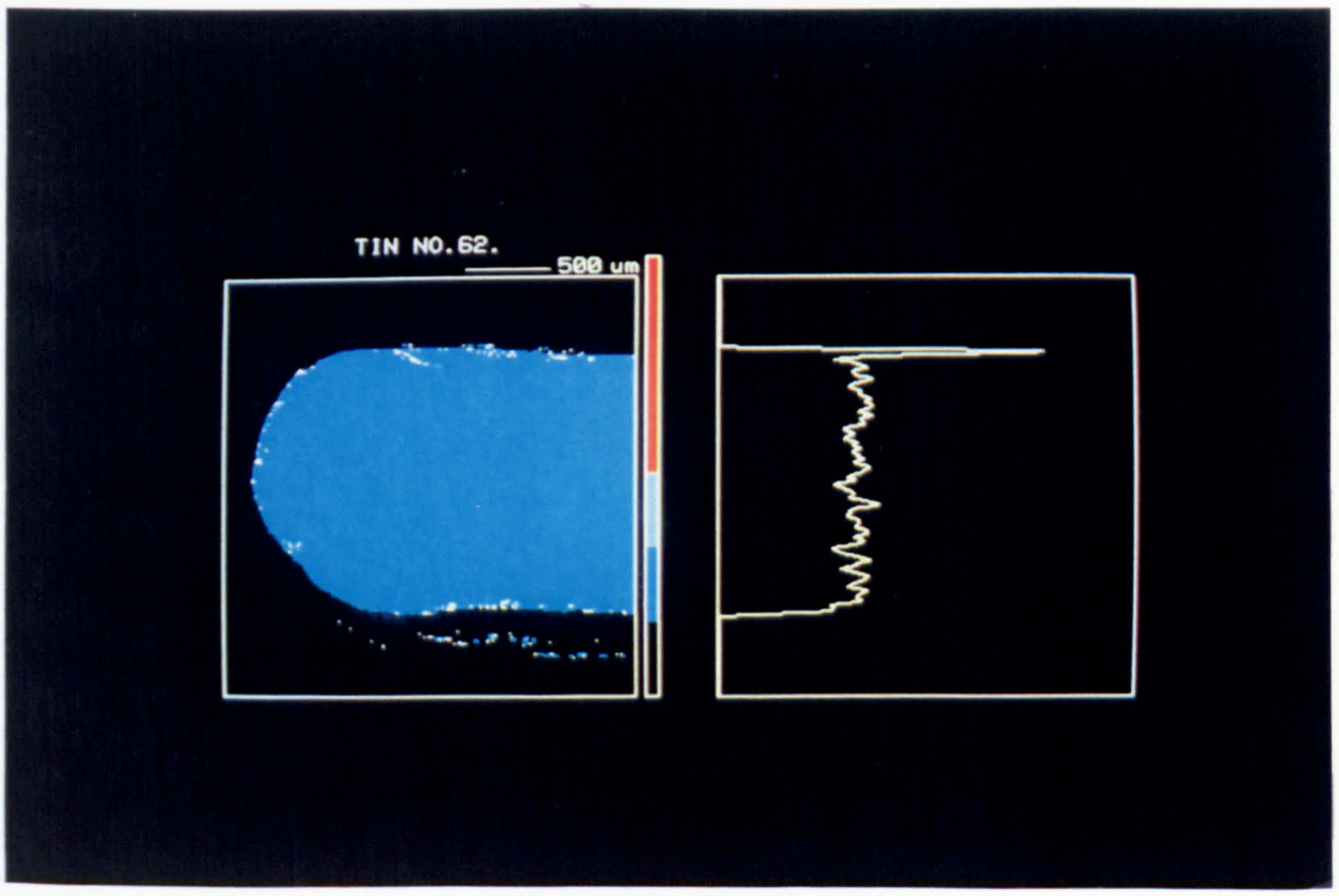

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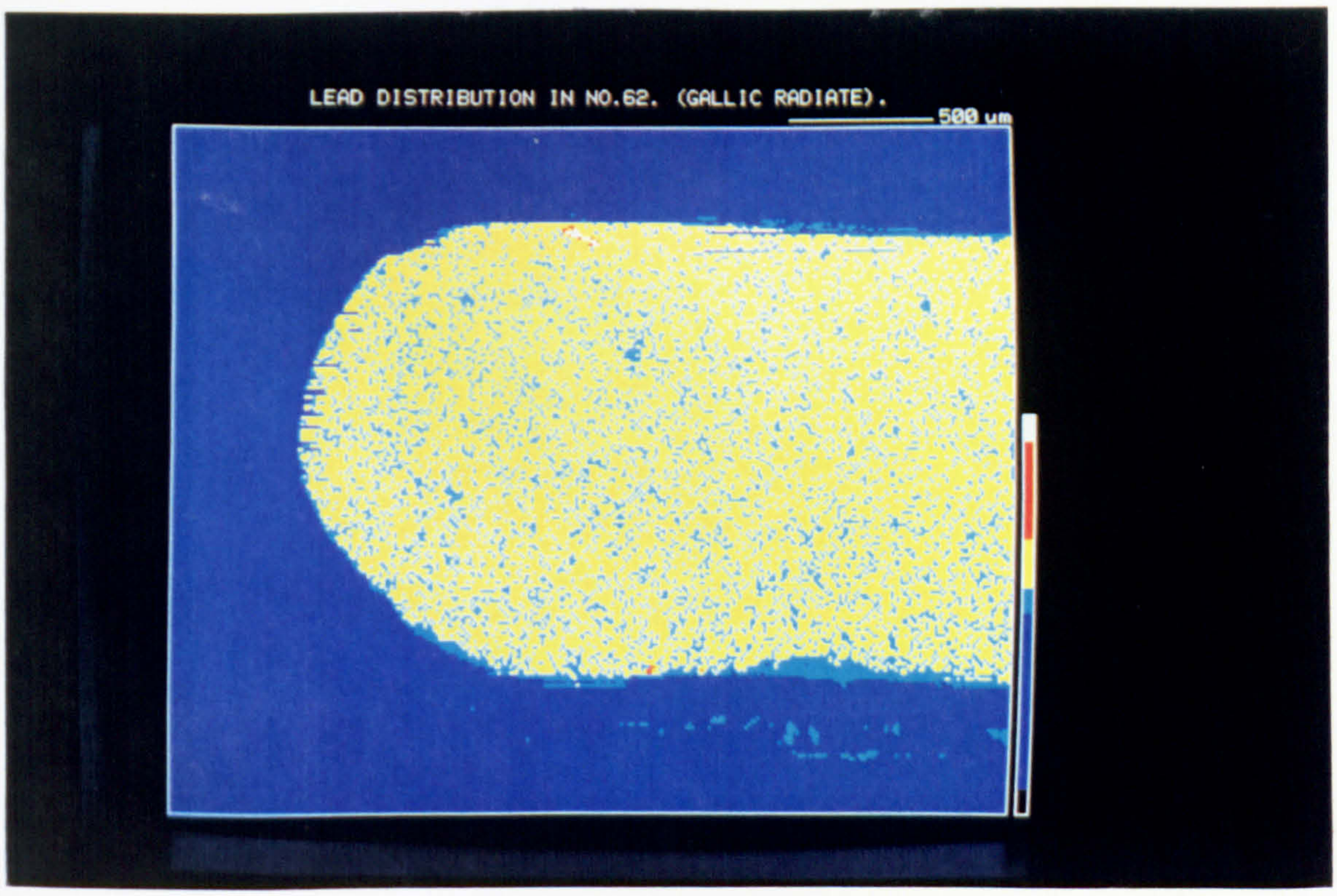
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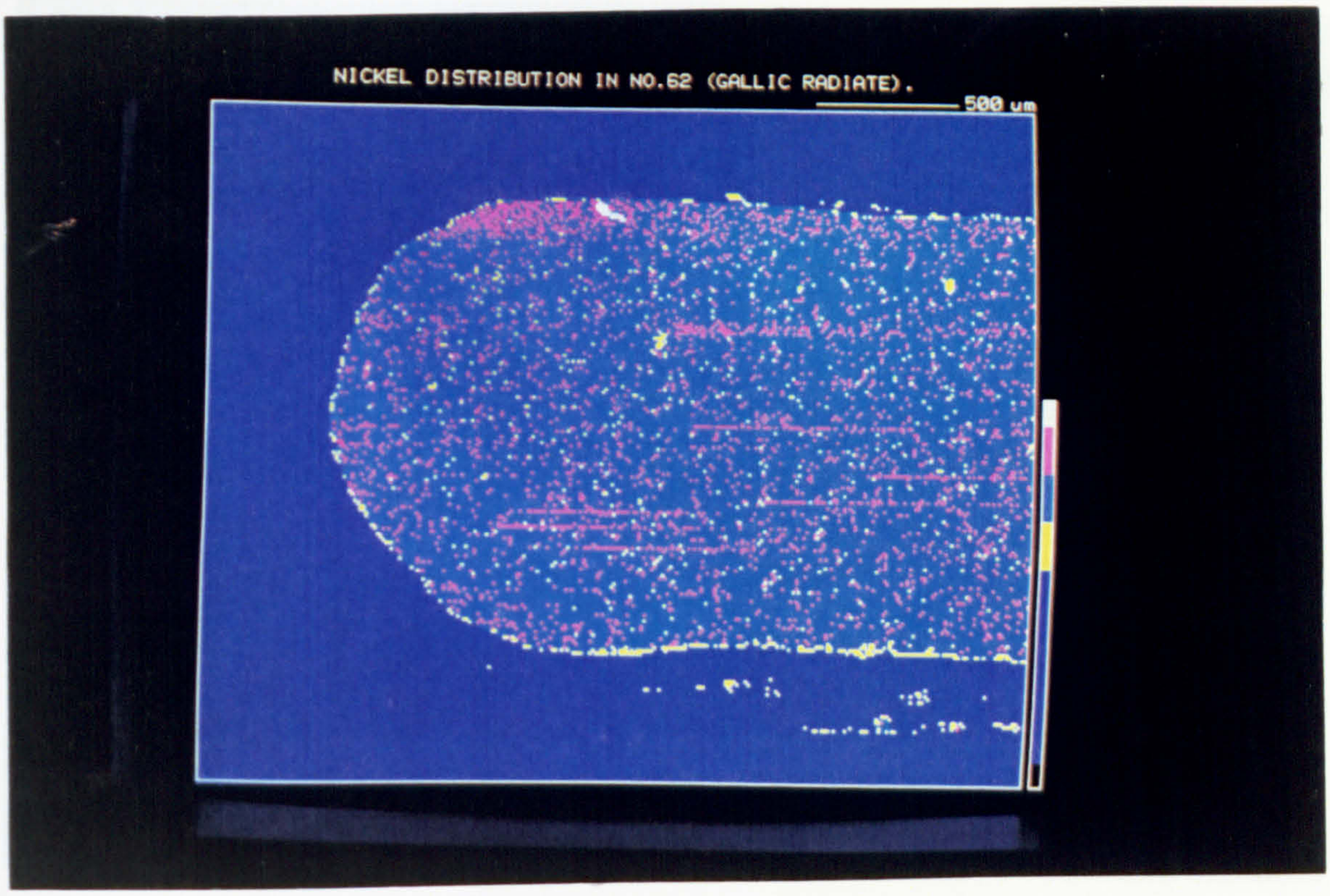
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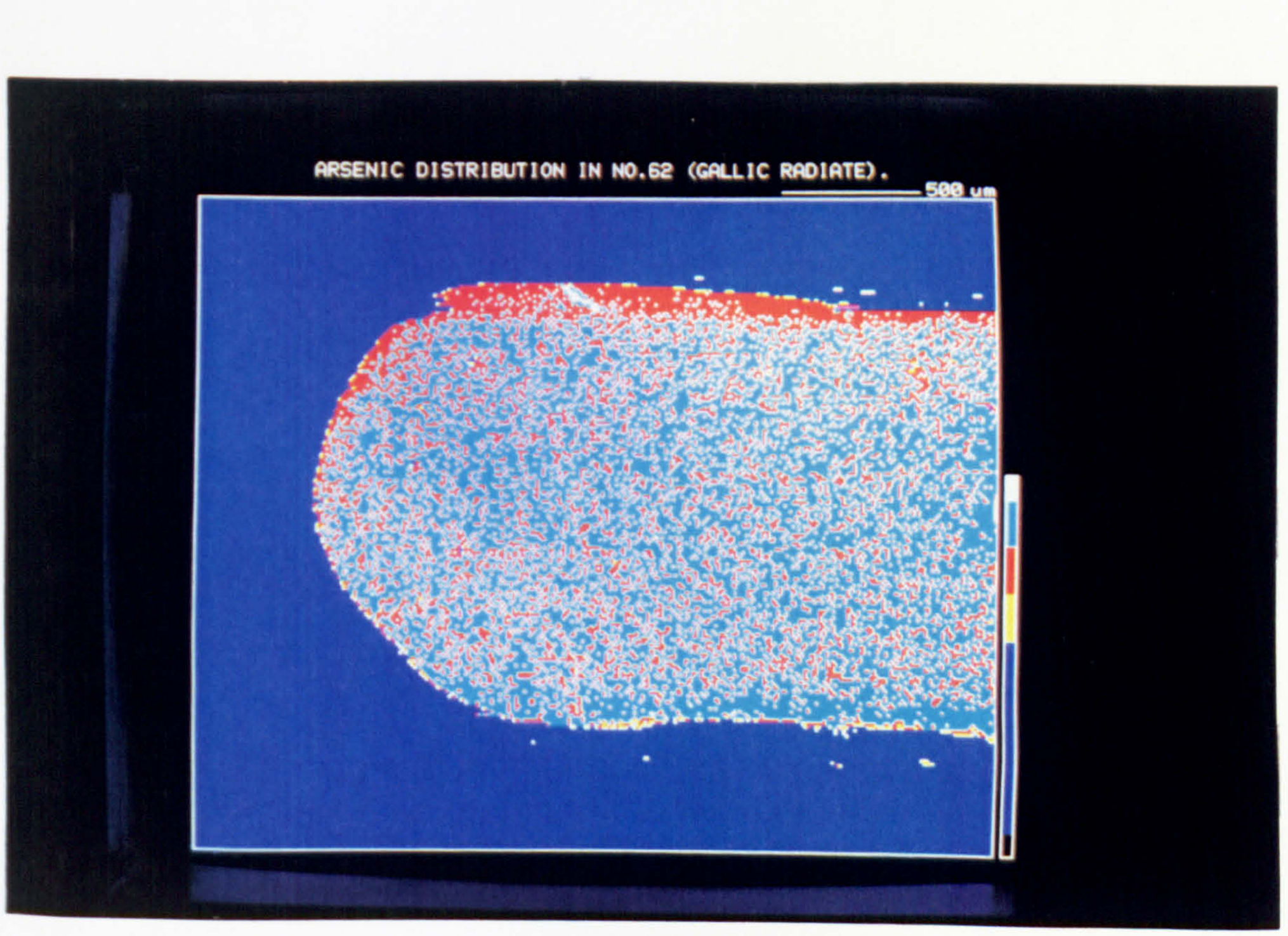
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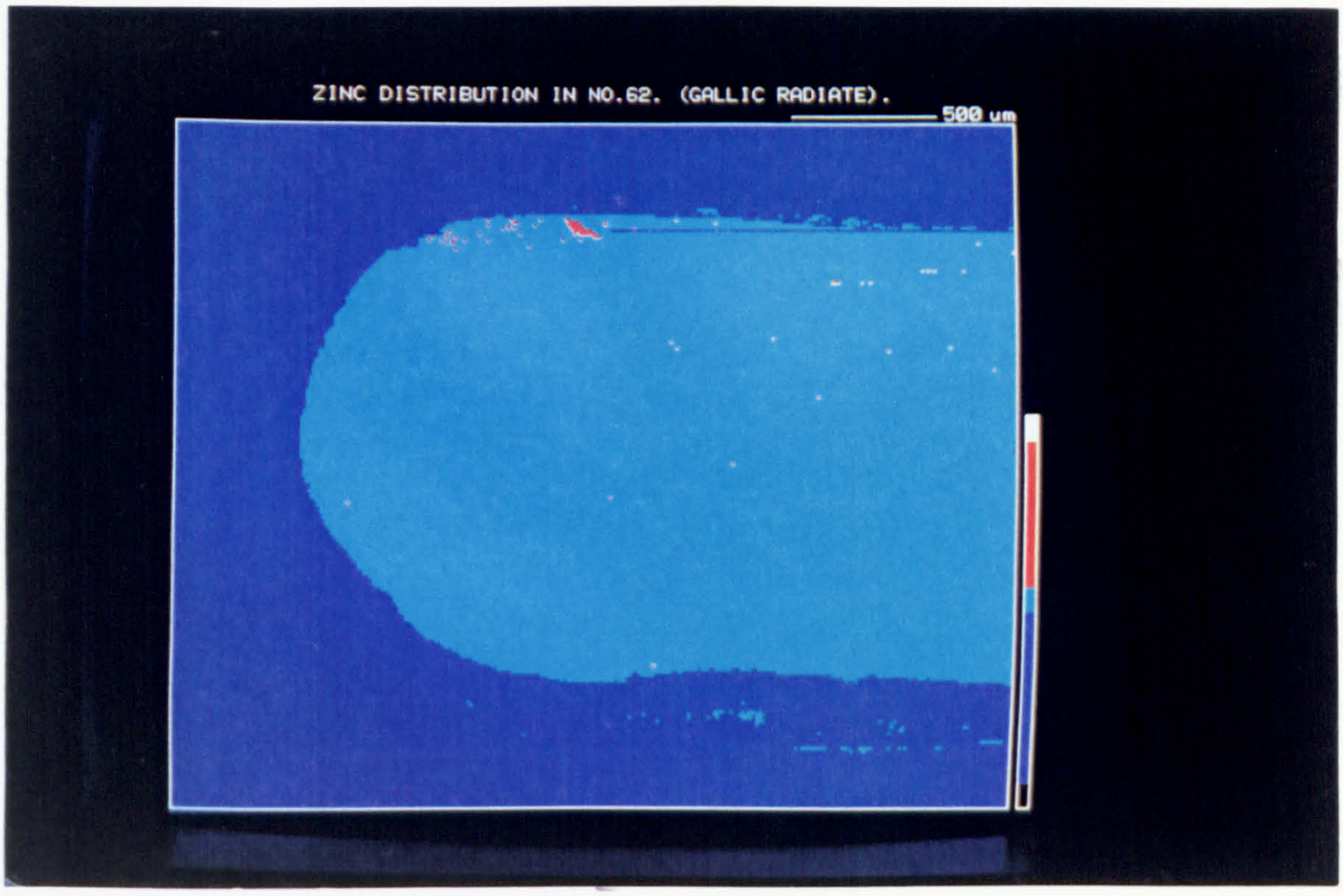

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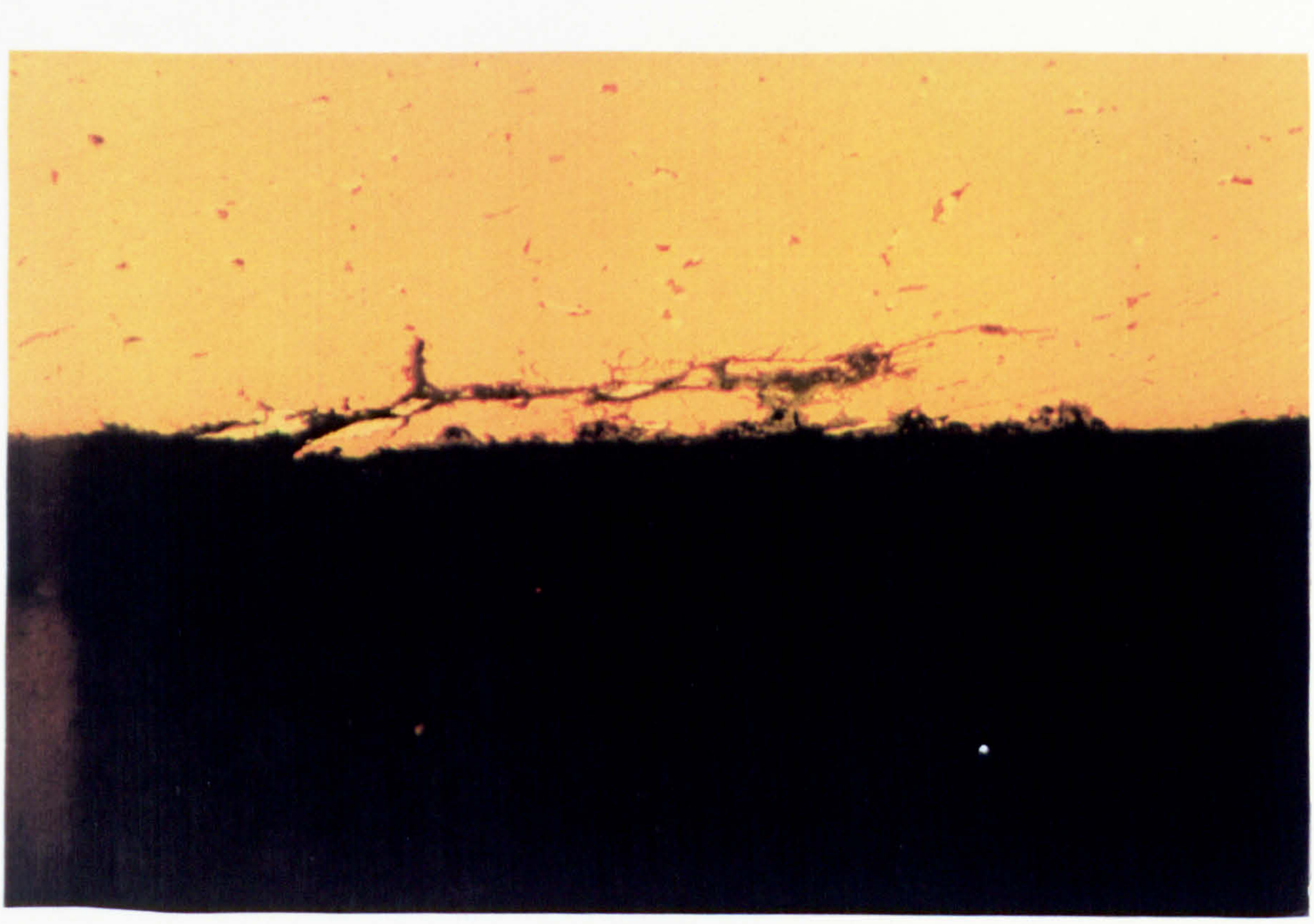

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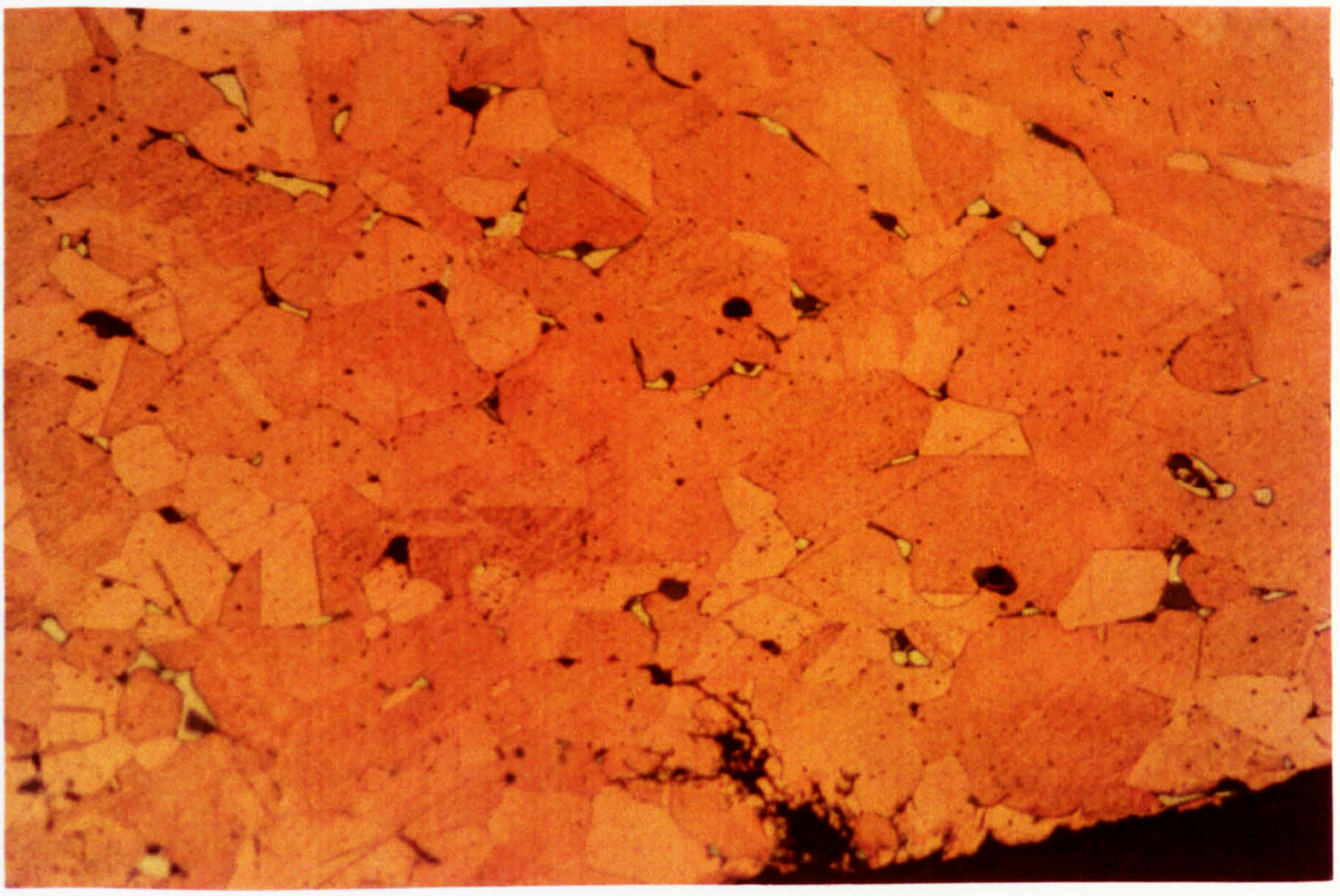

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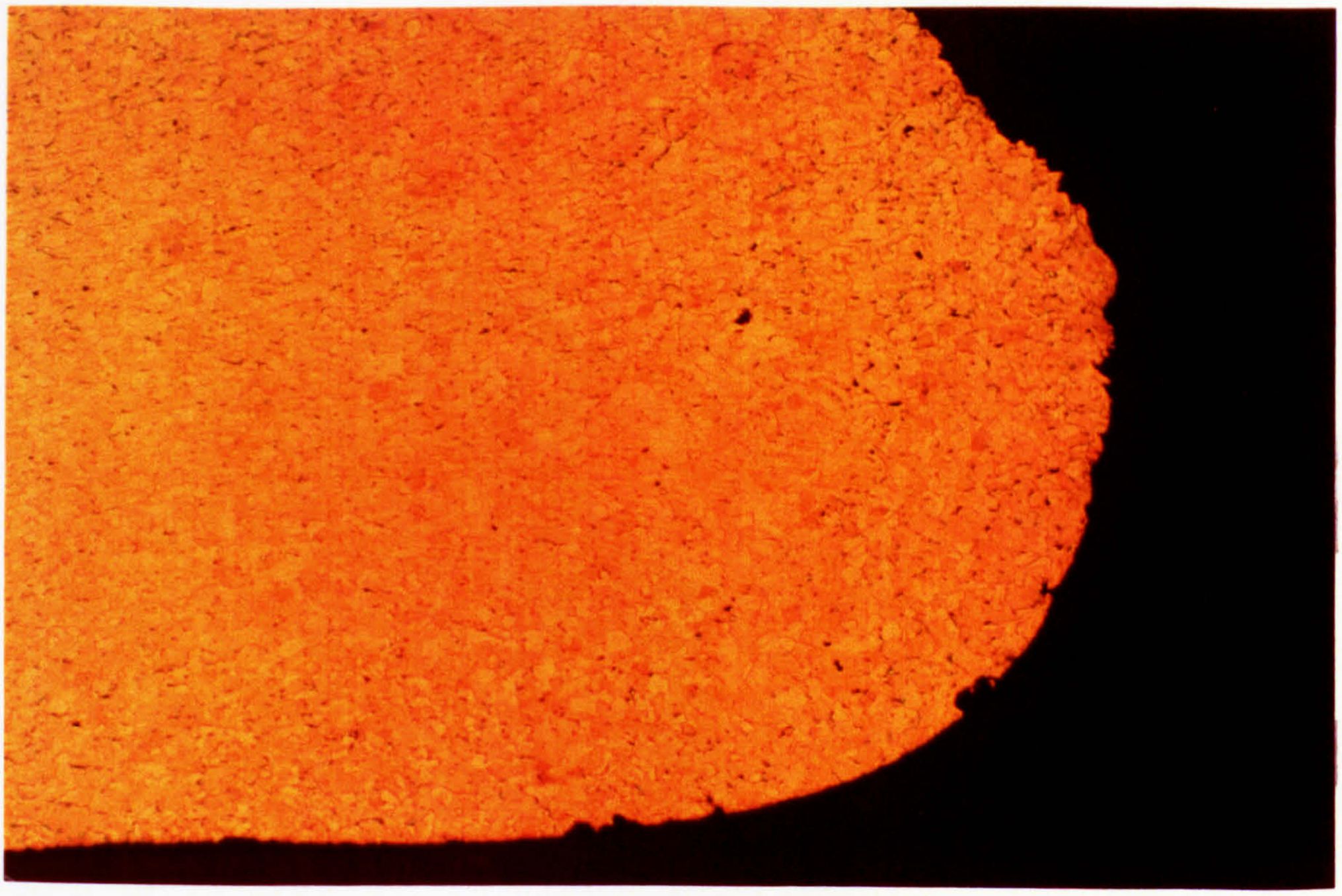

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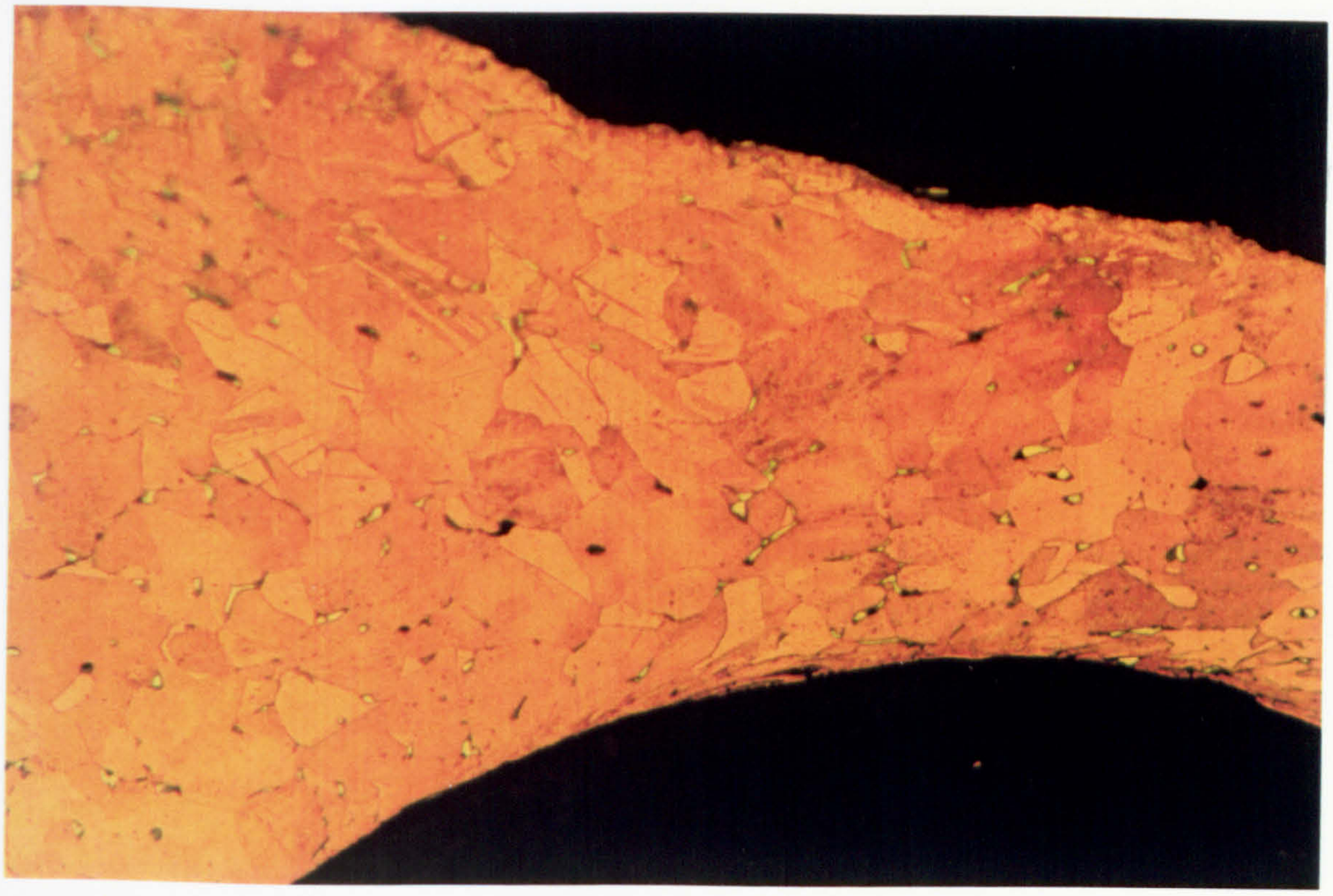

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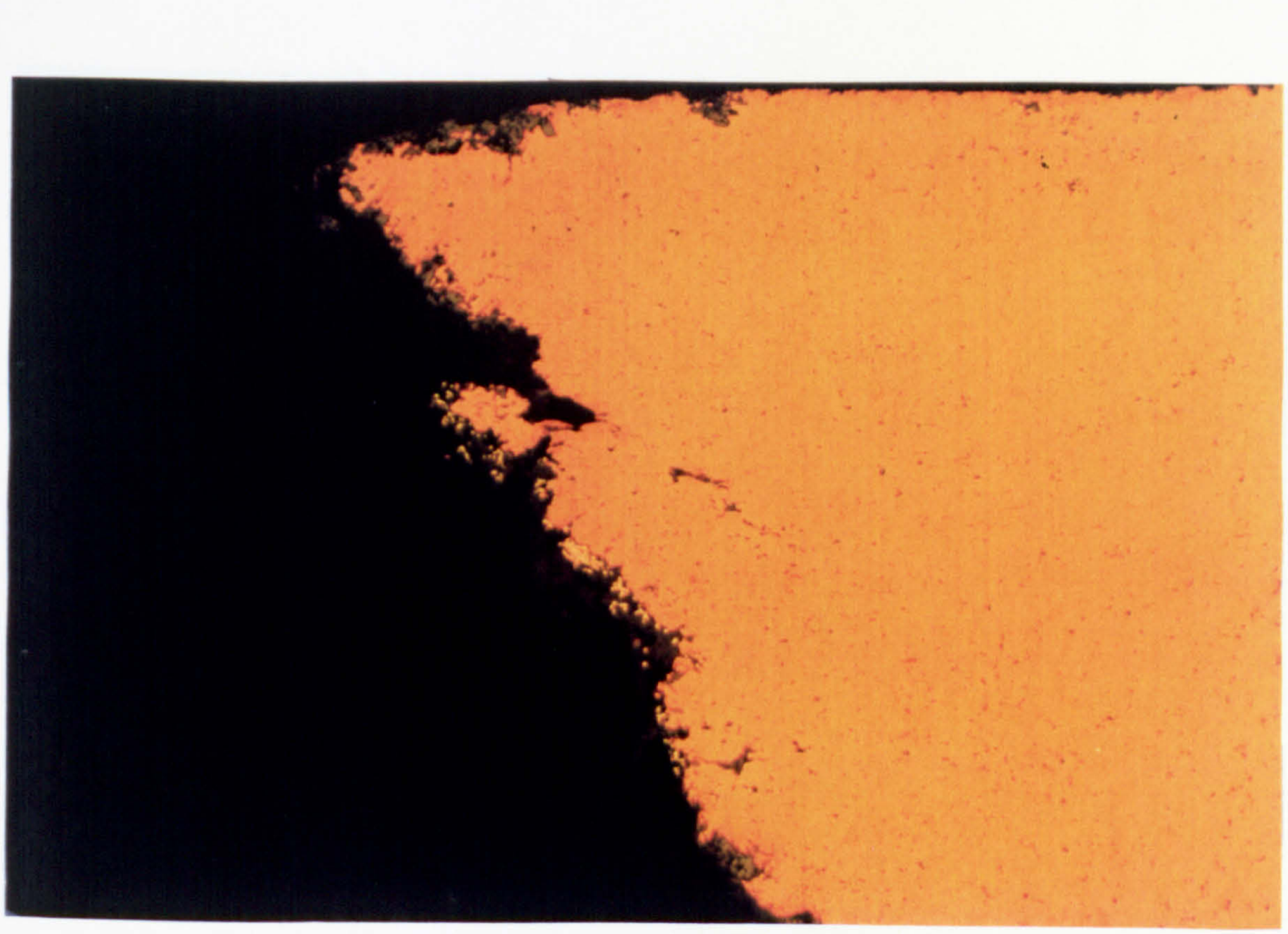

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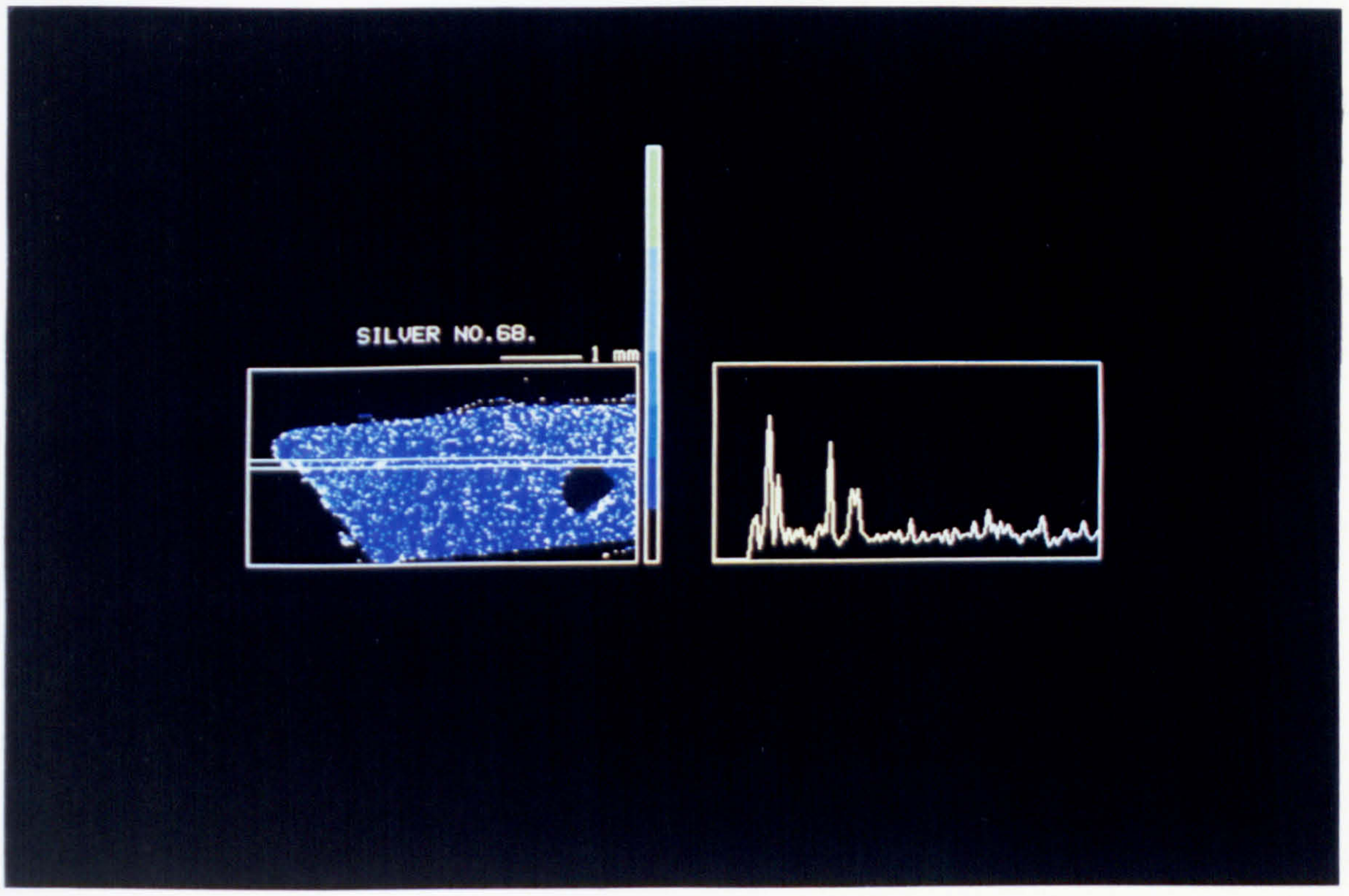

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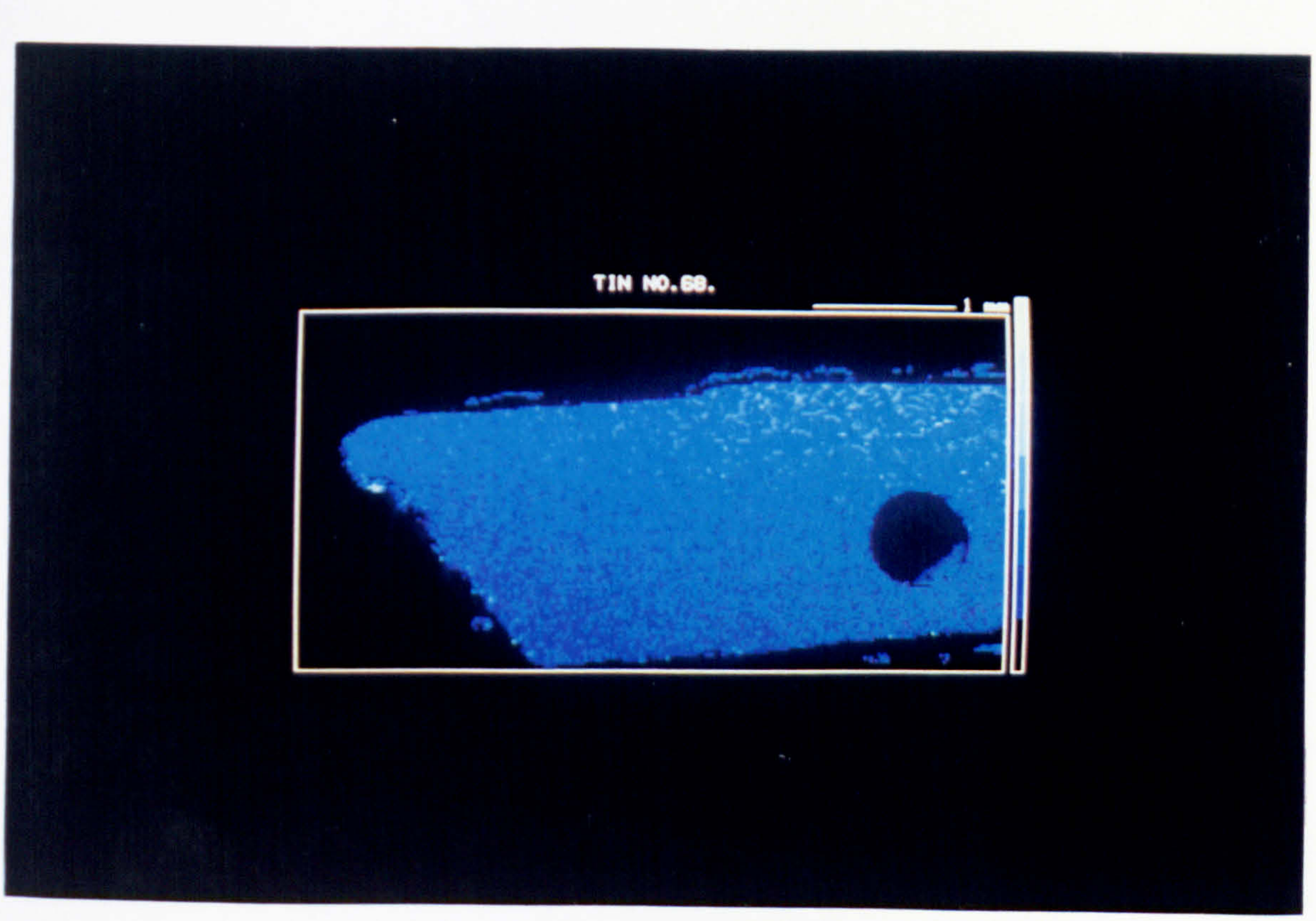

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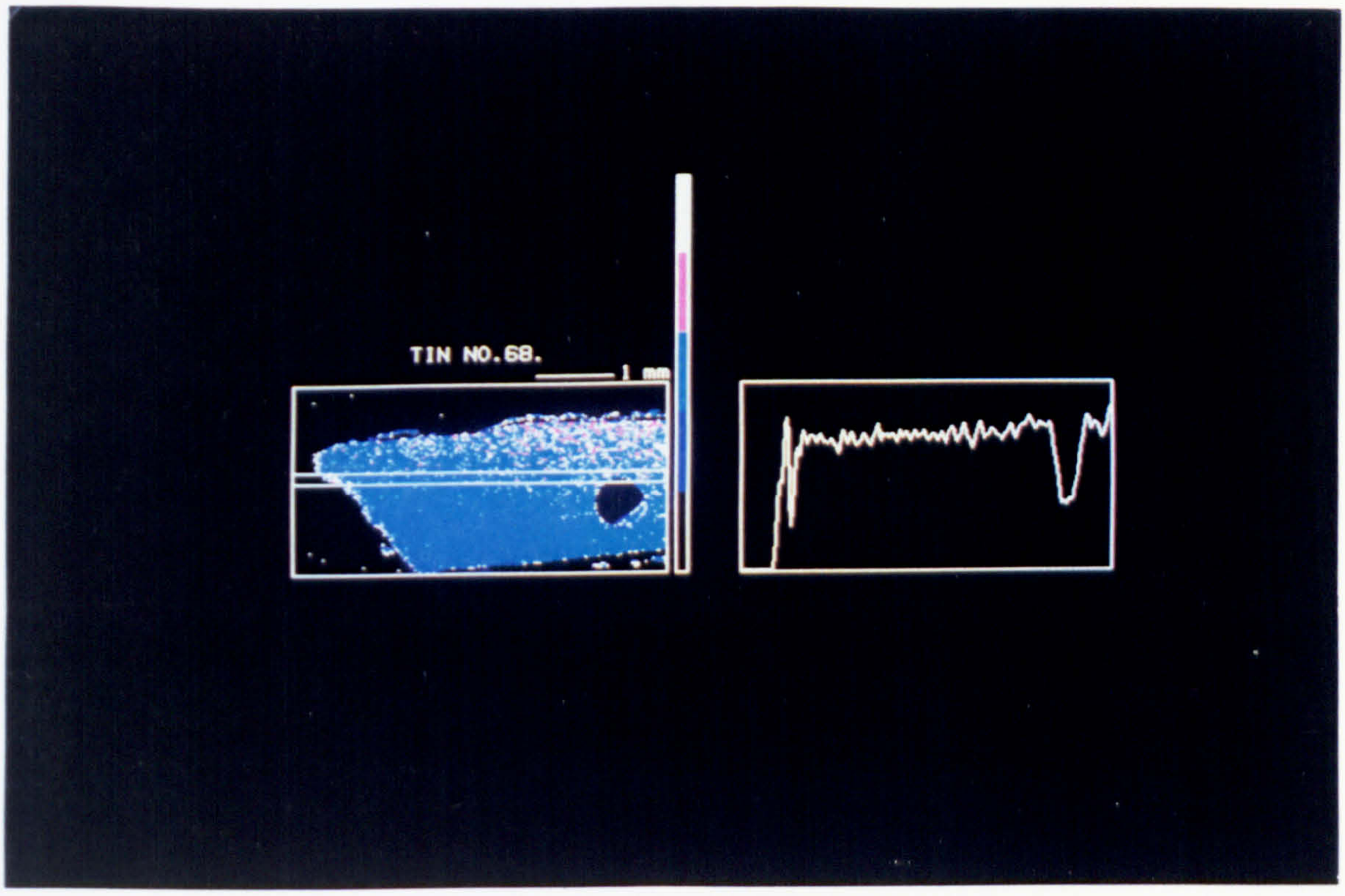

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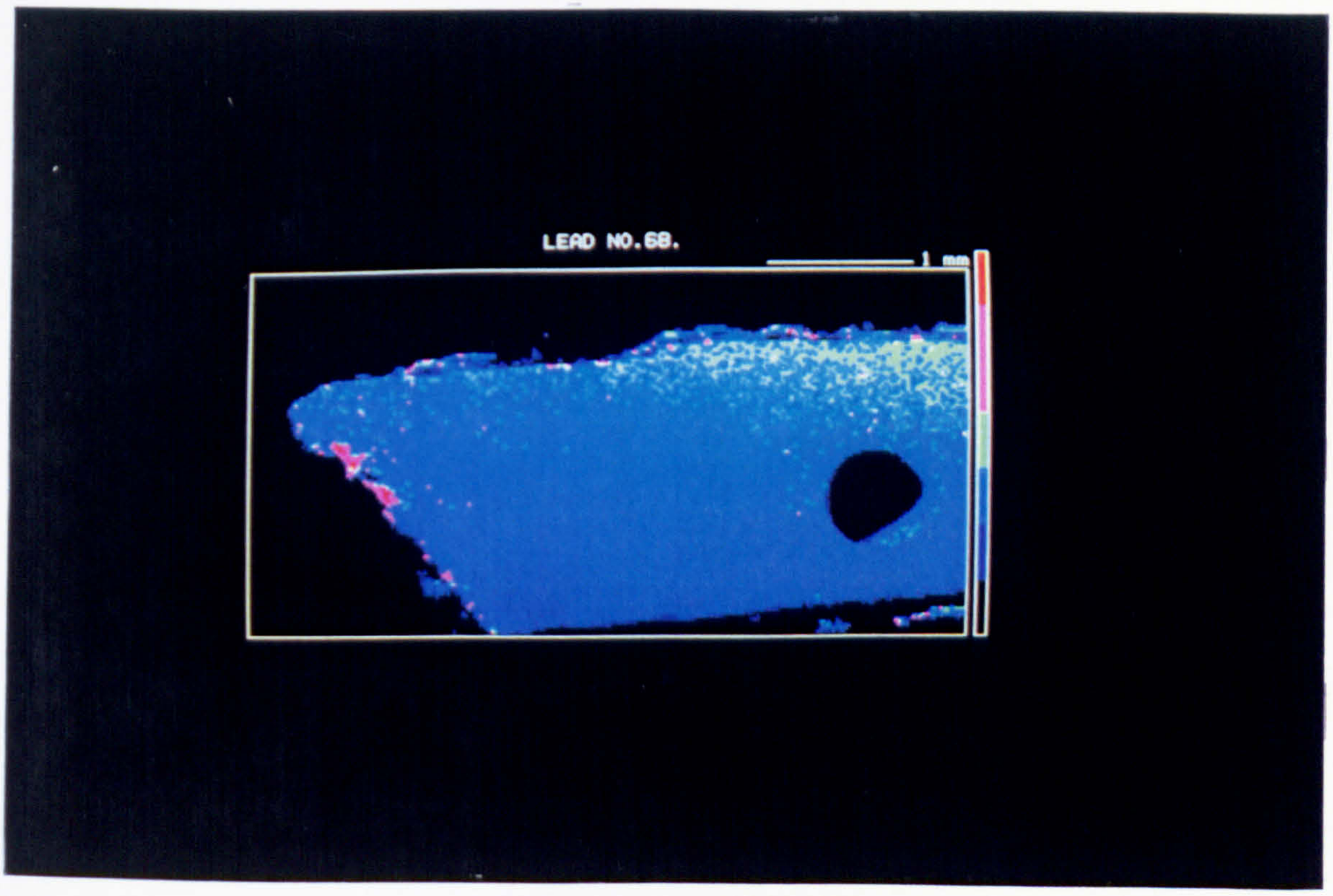

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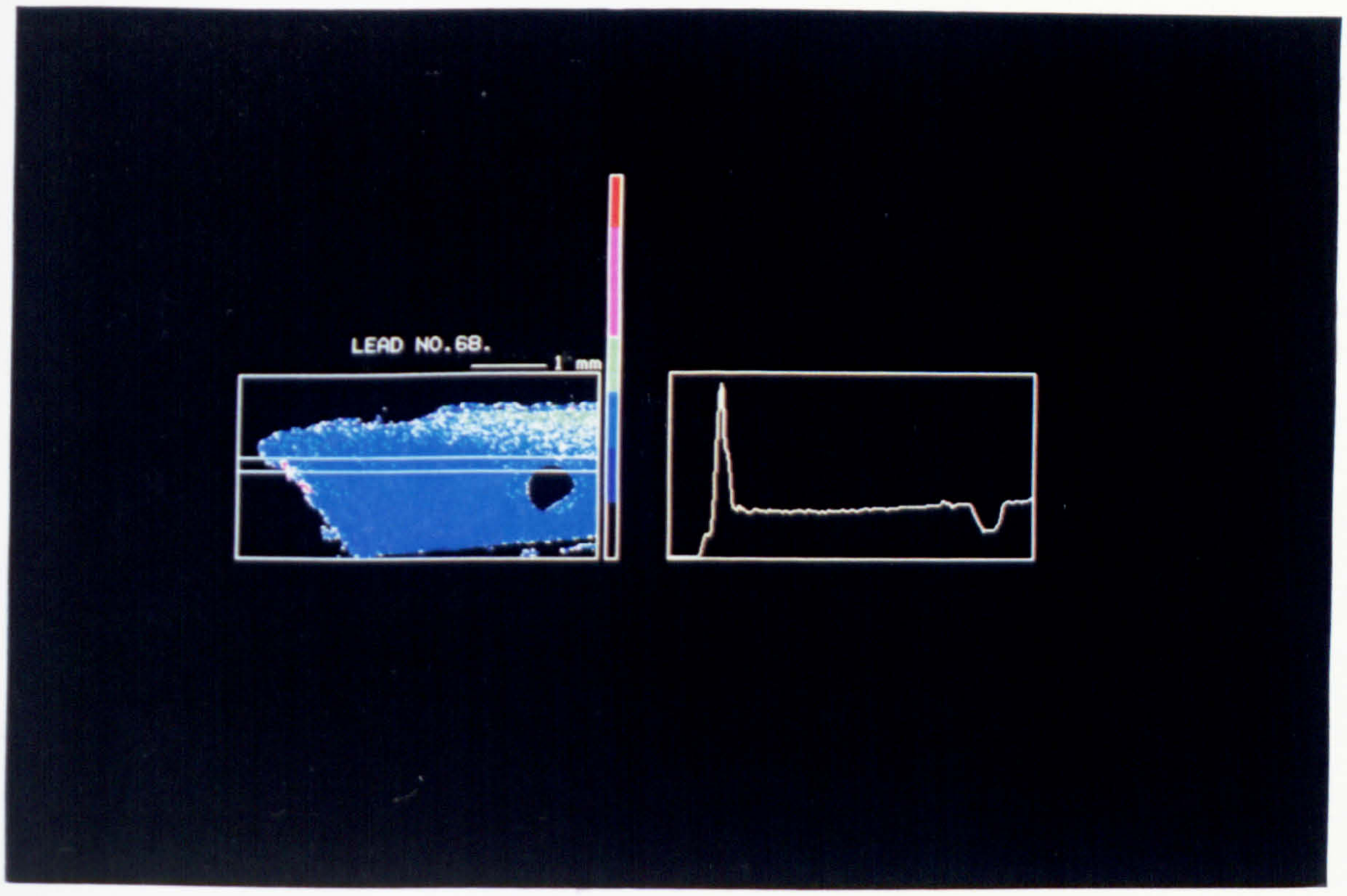

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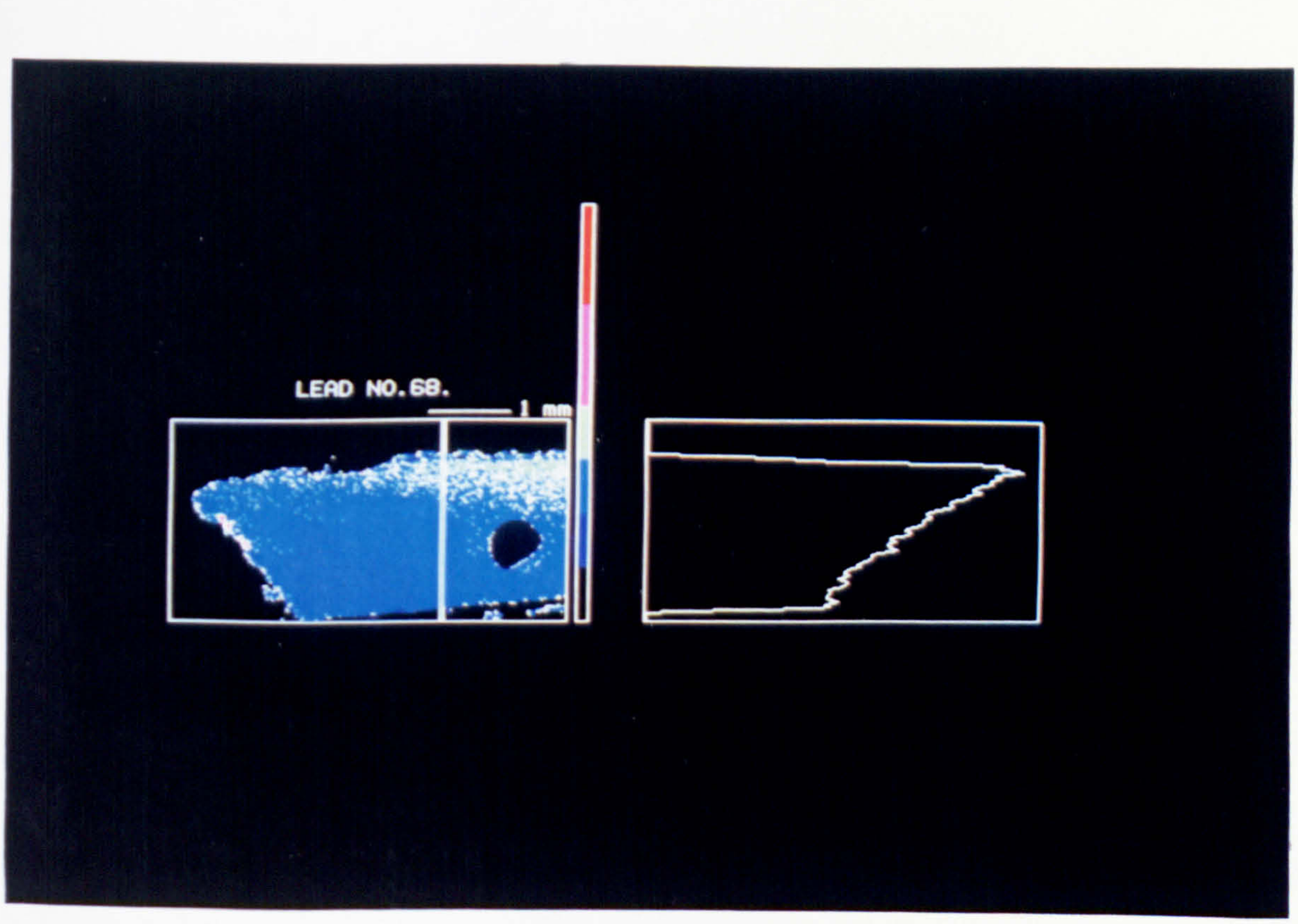

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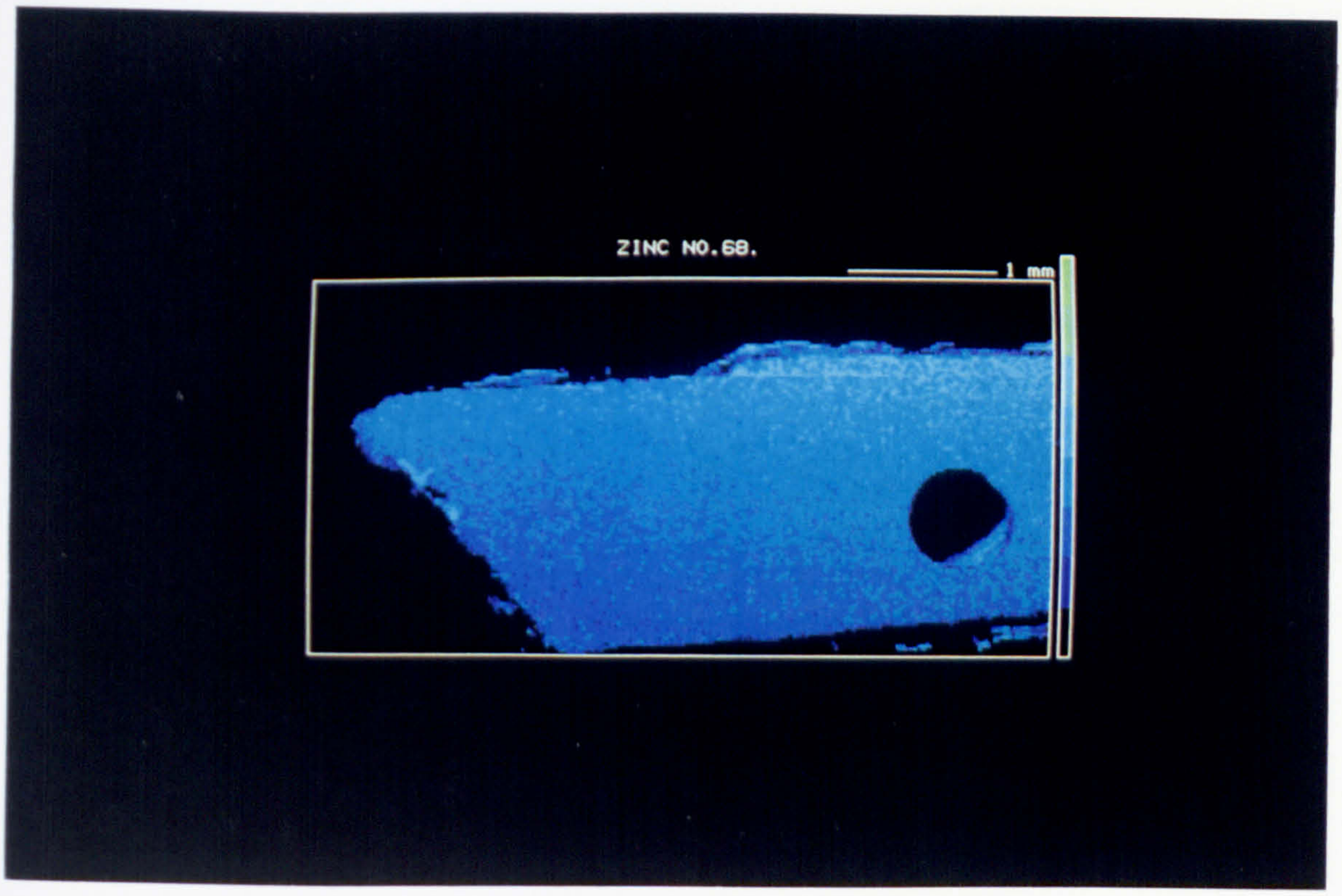

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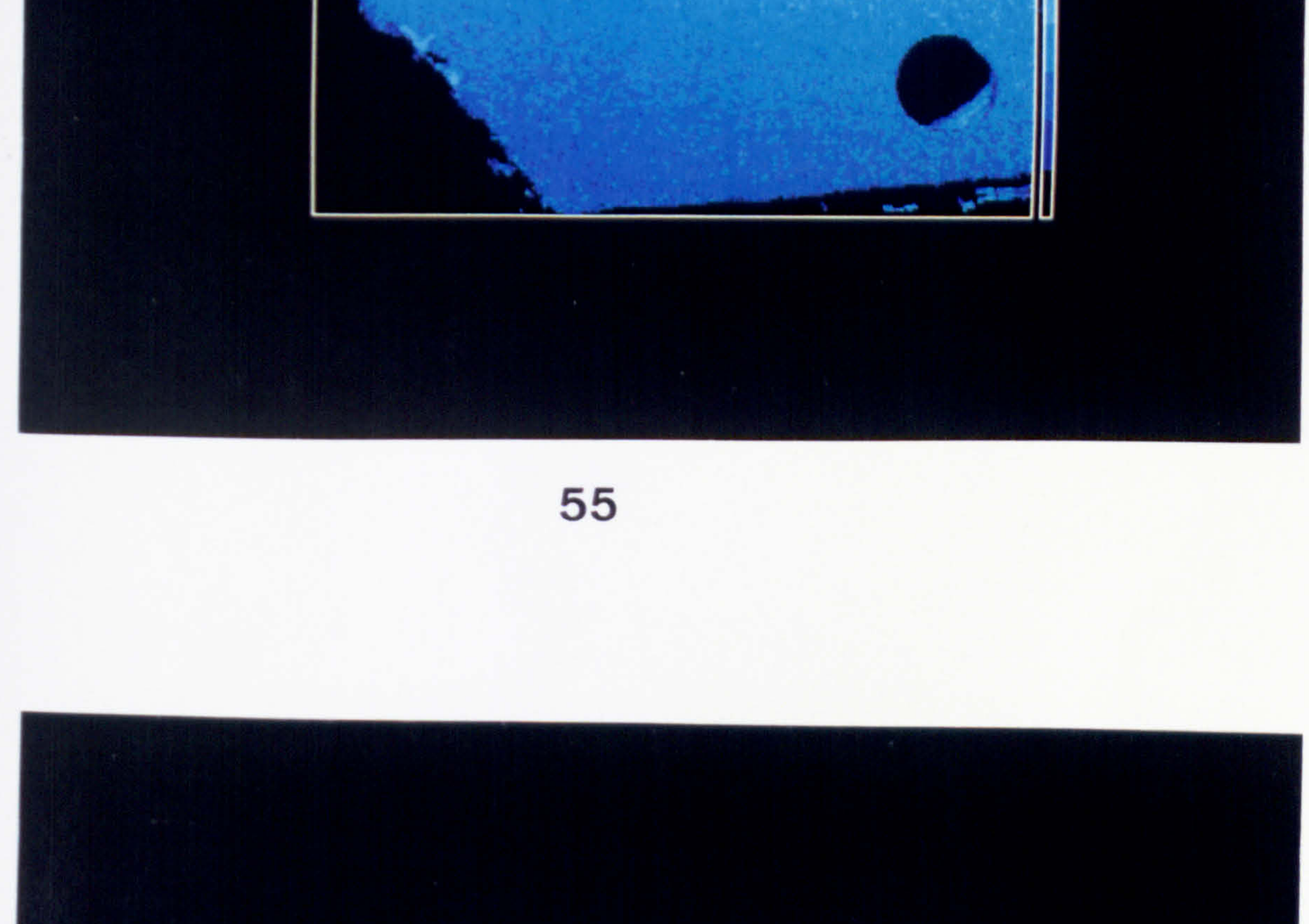

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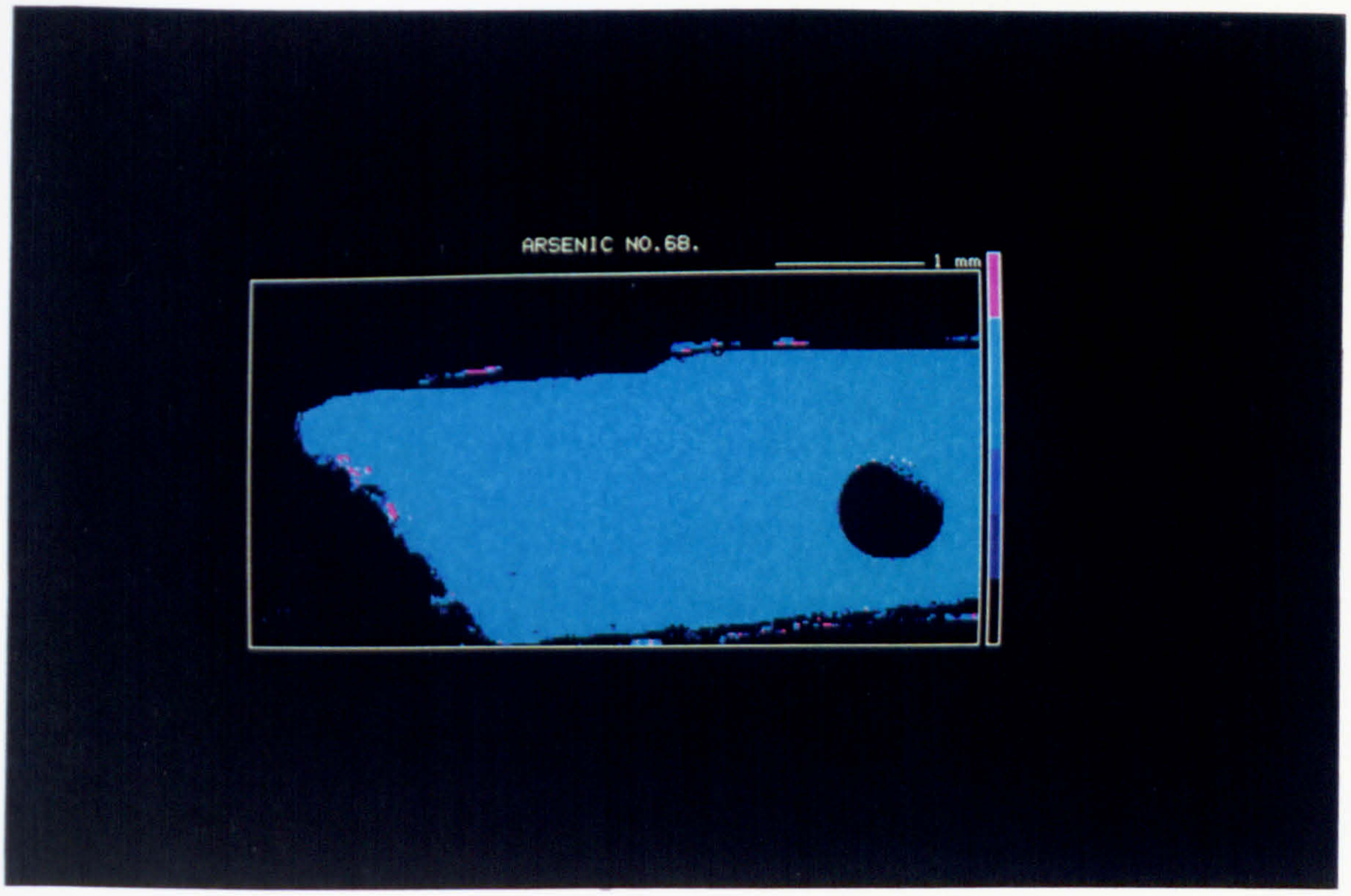
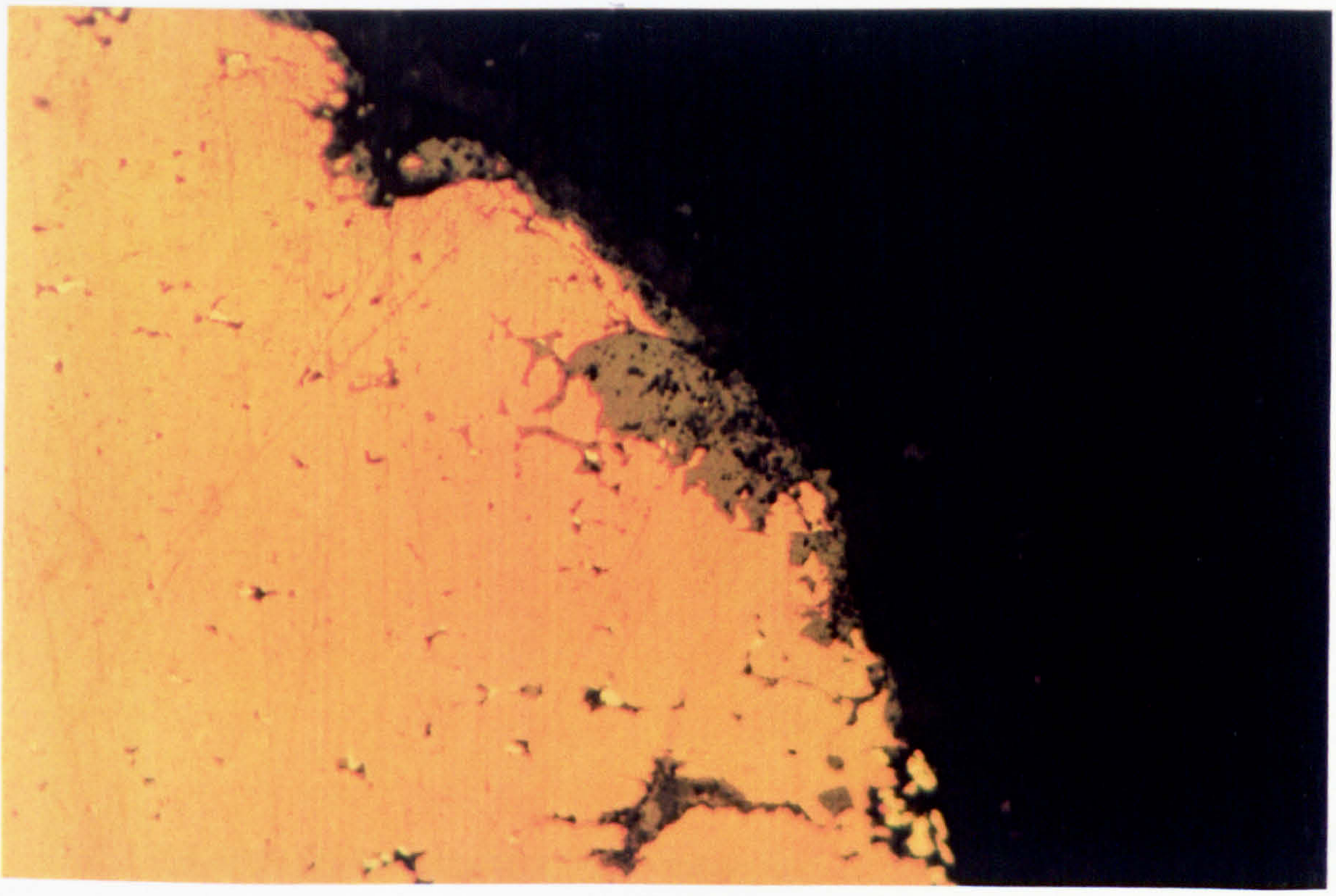
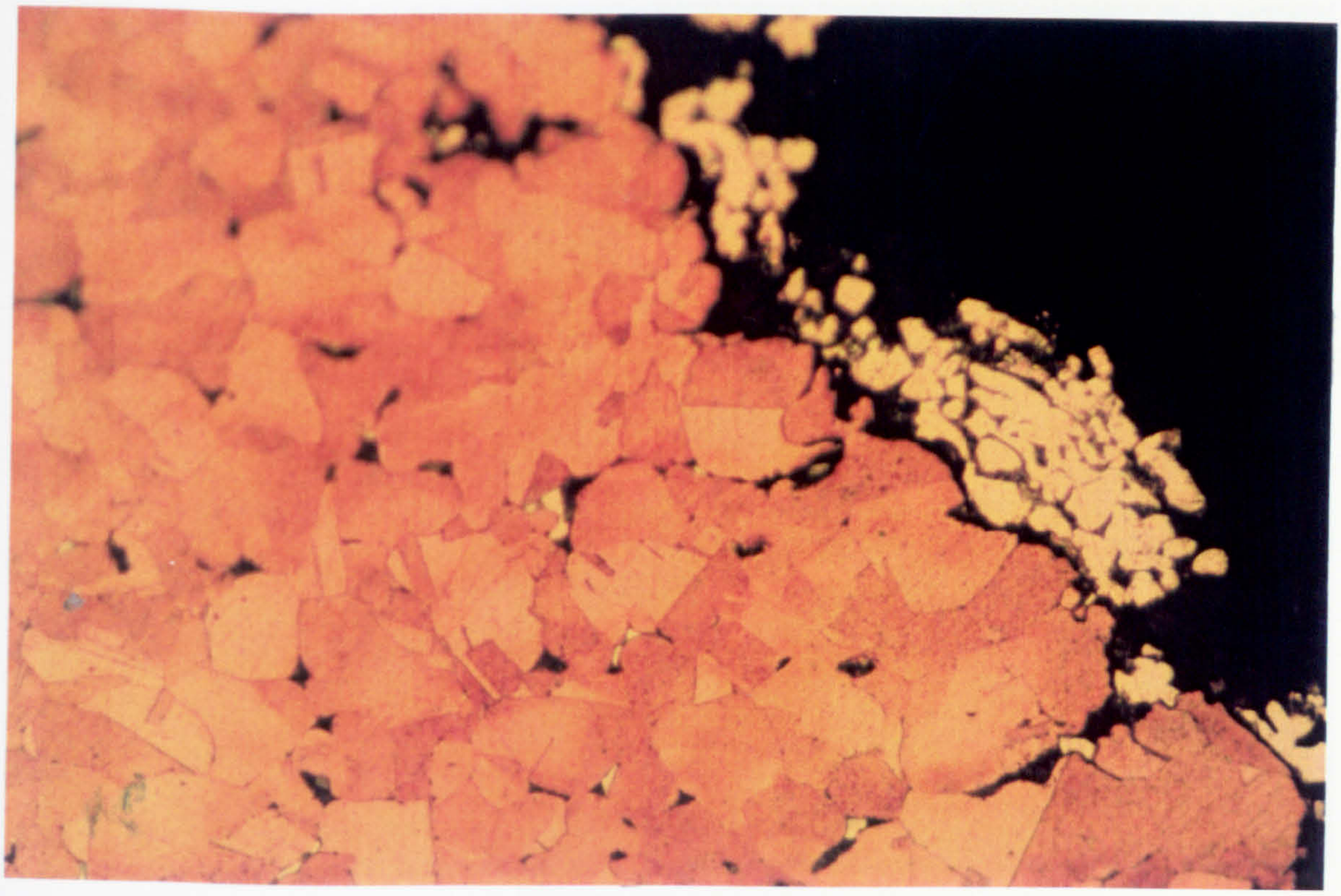


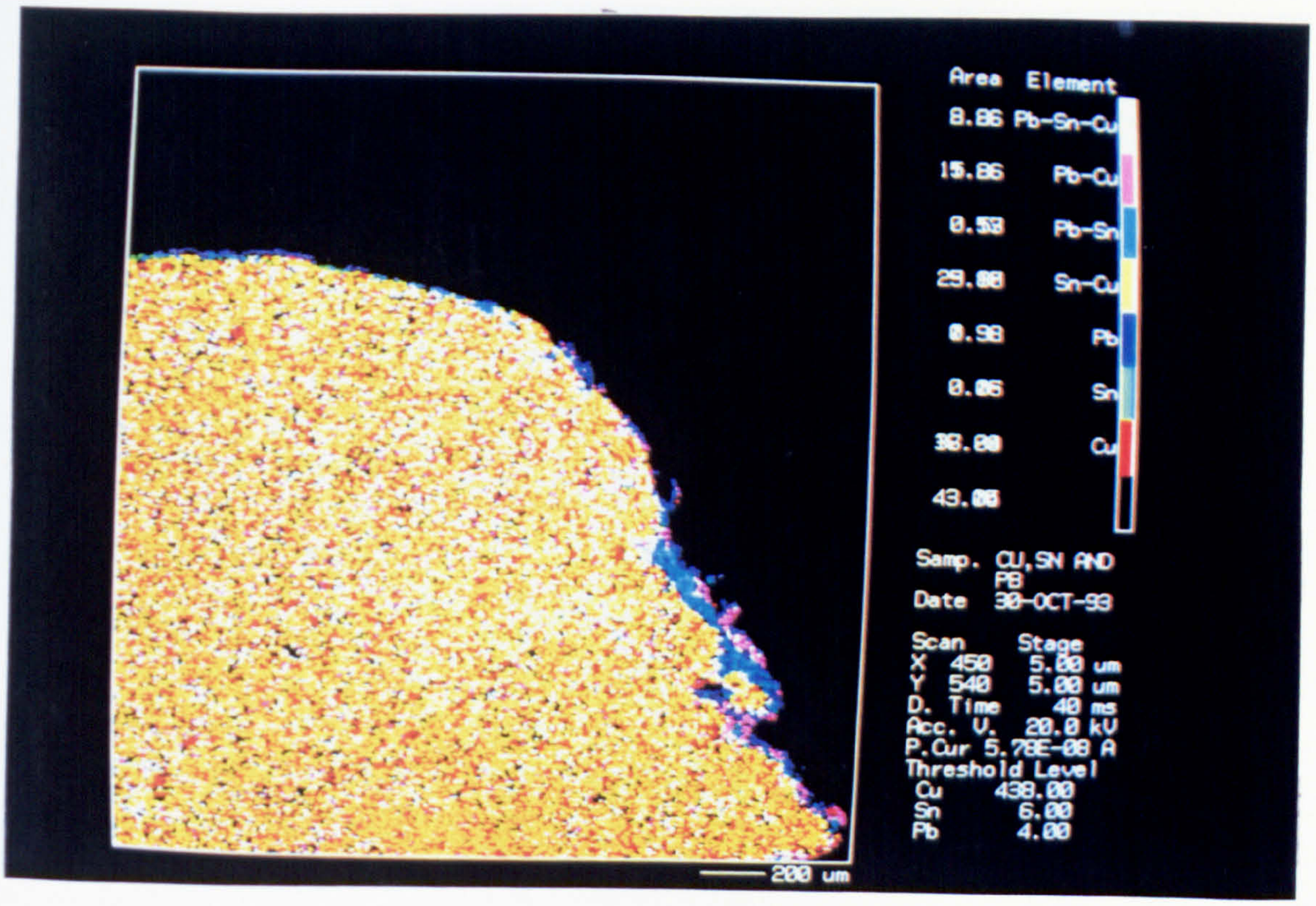
57



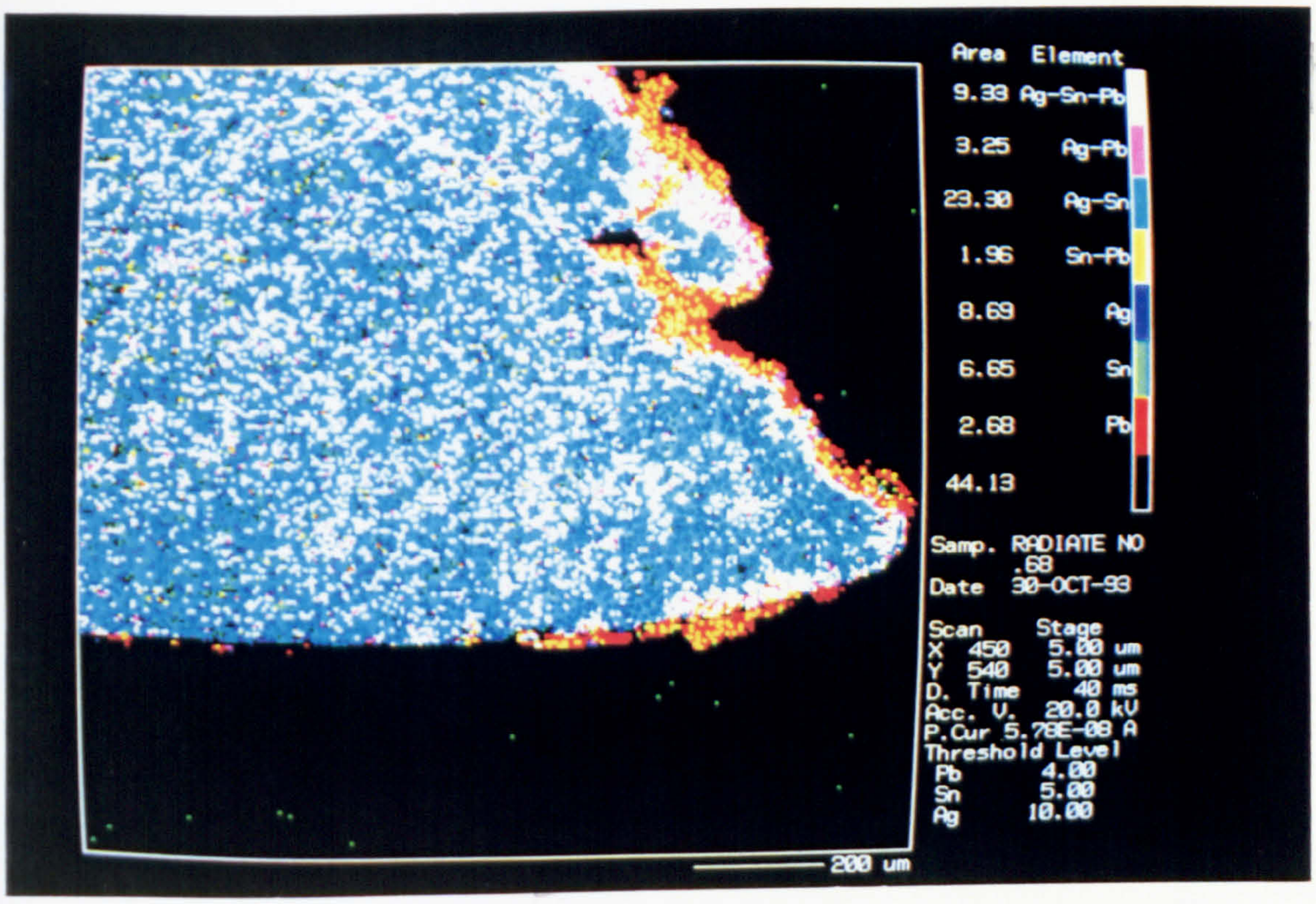
58



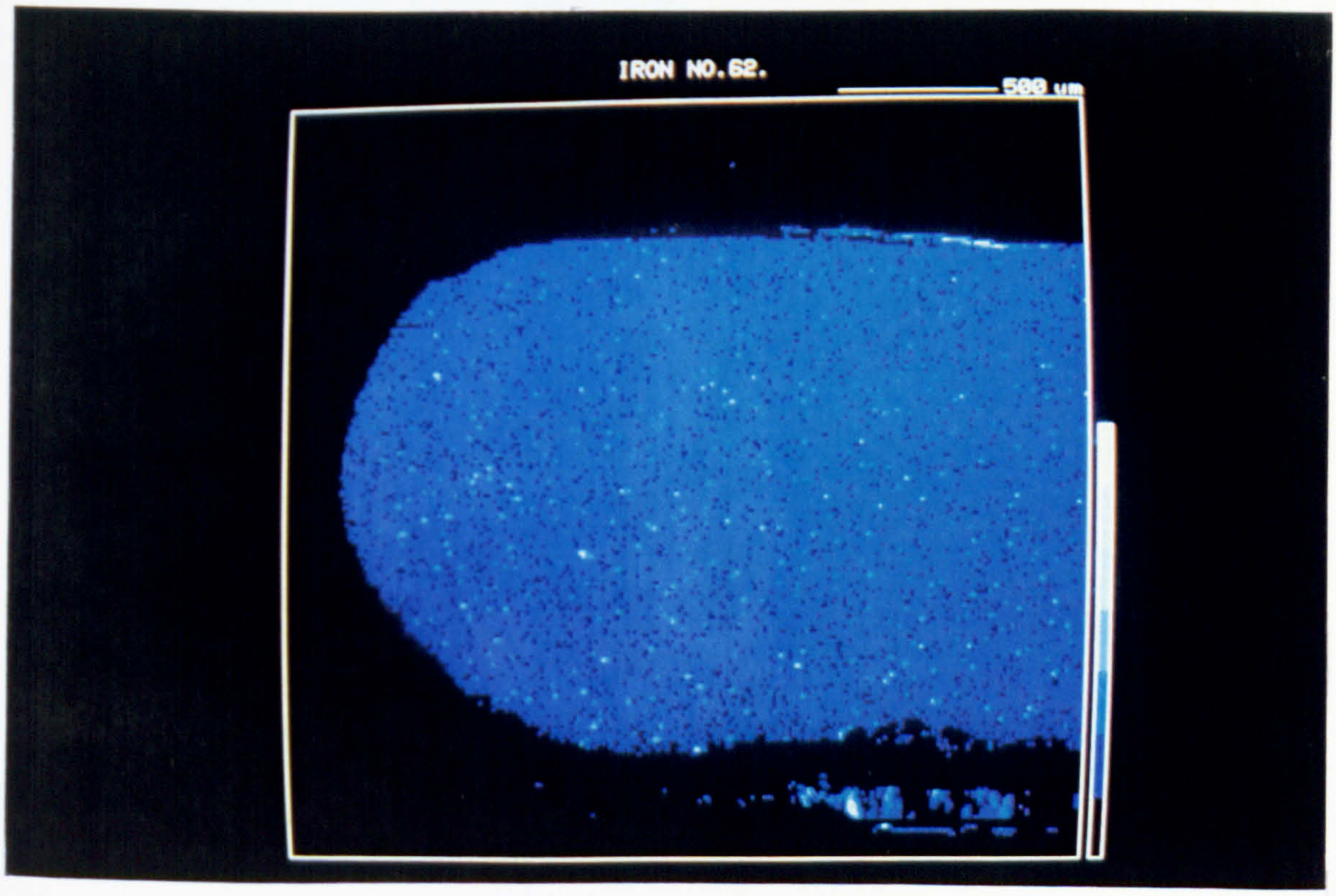
59


Area Element
8.86 Pb-Sn-Cu
15.86 Pb-Cu
0.53 Pb-Sn
29.00 Sn-Cu
0.93 Pb
0.05 Sn
38.00 Cu
43.00
Samp. CU,SN AND PB
Date 30-OCT-93
Scan Stage
X 450 5.00 um
Y 540 5.00 um
D. Time 40 ms
Acc. V. 20.0 kV
P.Cur 5.78E-08 A
Threshold Level
Cu 438.00
Sn 6.00
Pb 4.00
200 um

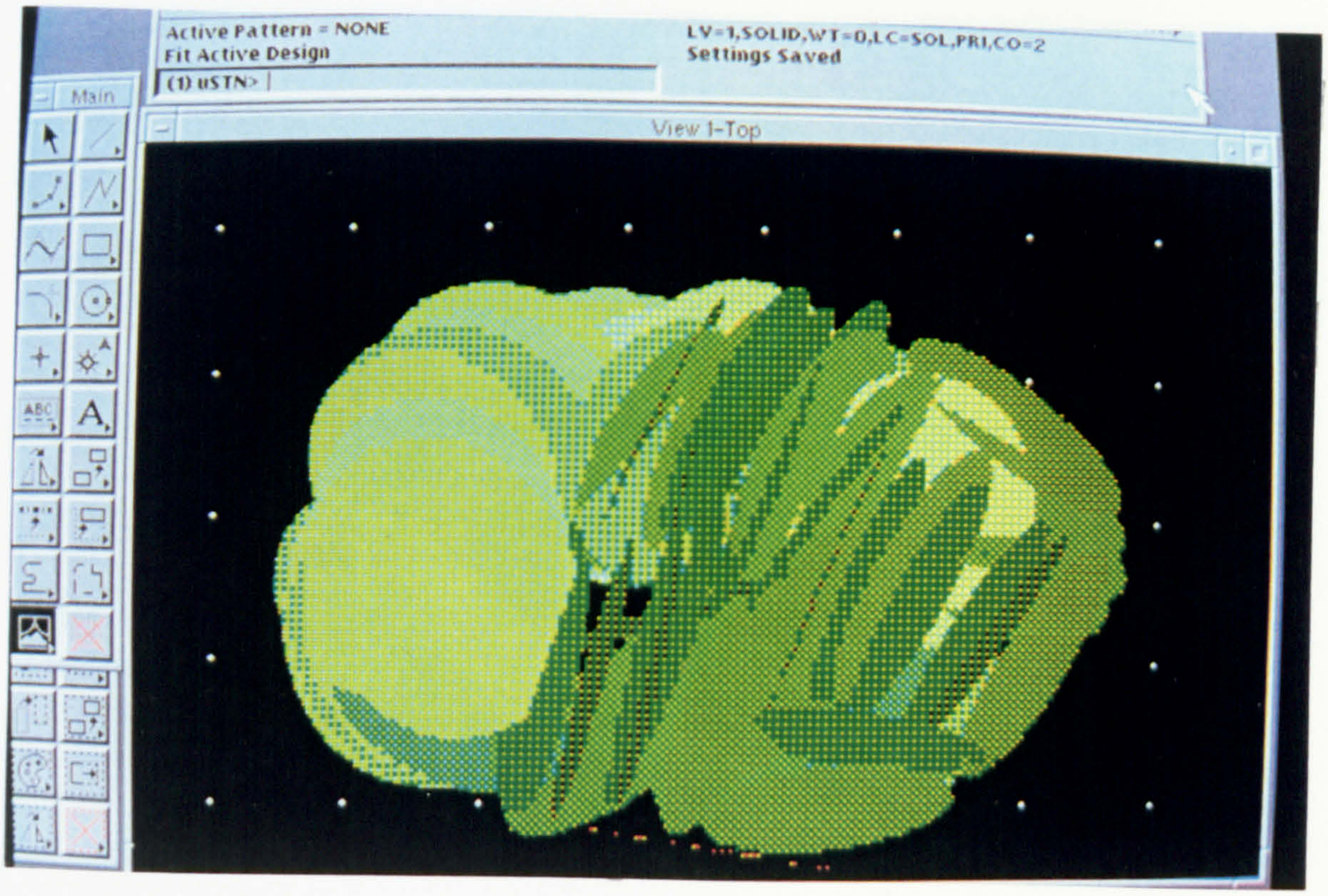
60


Area Element
9.33 Ag-Sn-Pb
3.25 Ag-Pb
23.30 Ag-Sn
1.96 Sn-Pb
8.69 Ag
6.65 Sn
2.68 Pb
44.13
Samp. RADIATE NO .68
Date 30-OCT-93
Scan Stage
X 450 5.00 um
Y 540 5.00 um
D. Time 40 ms
Acc. V. 20.0 kV
P.Cur 5.78E-08 A
Threshold Level
Pb 4.00
Sn 5.00
Ag 10.00
200 um

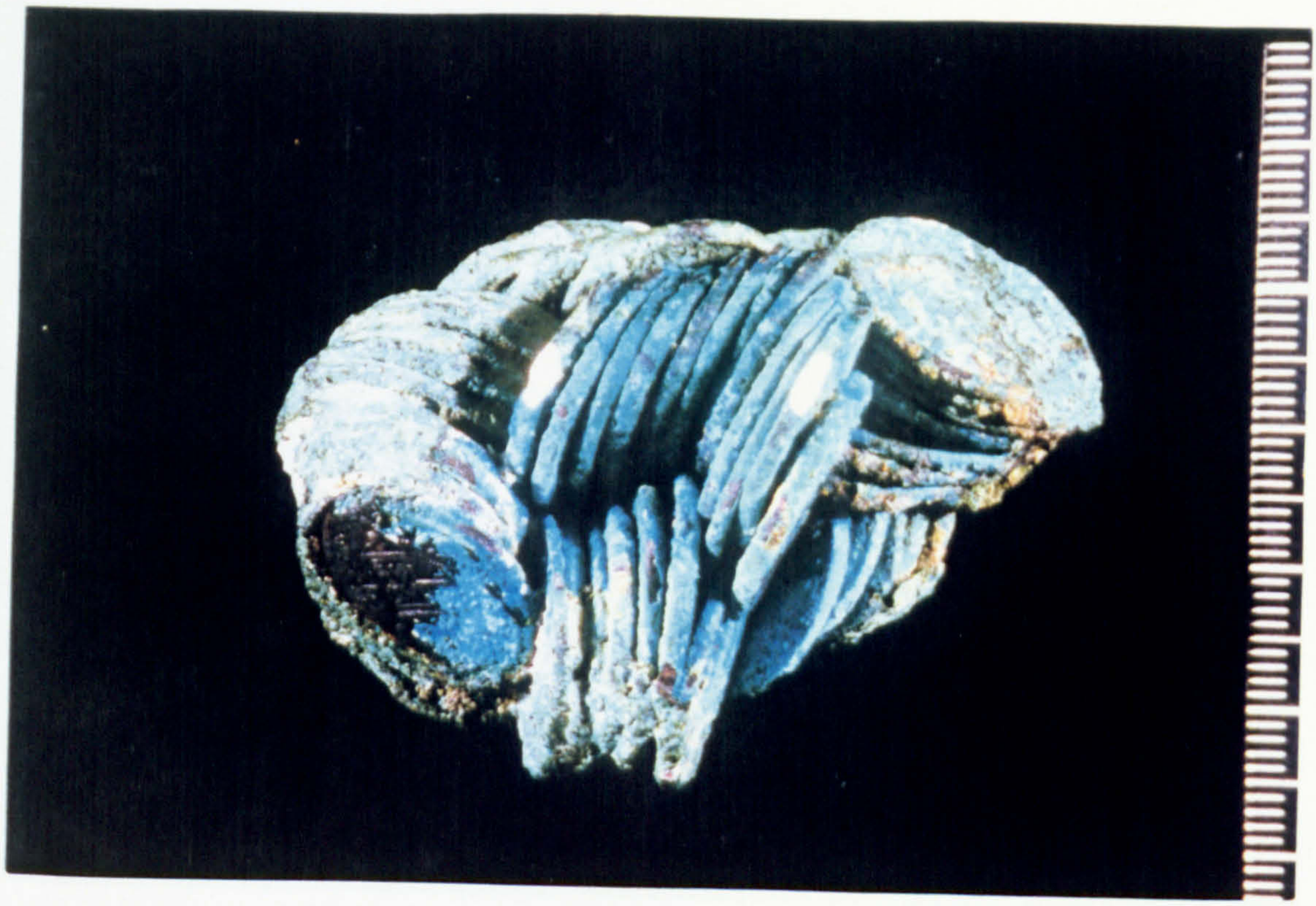
61


IRON NO.62.
500 um

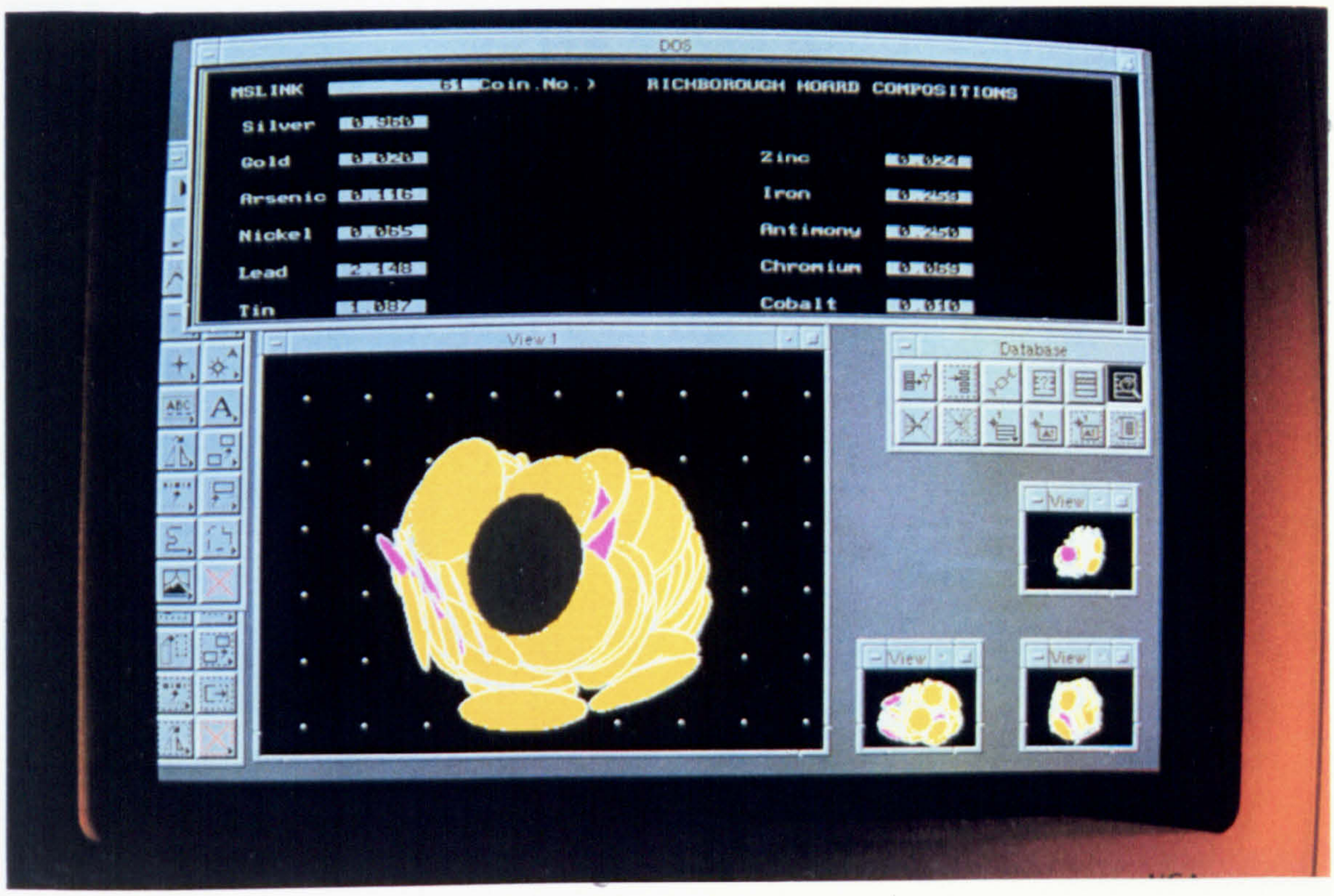
62


Active Pattern = NONE
Fit Active Design
(1) uSTN>
LV=1,SOLID,WT=0,LC=SOL,PRI,CO=2
Settings Saved
Main
View 1-Top

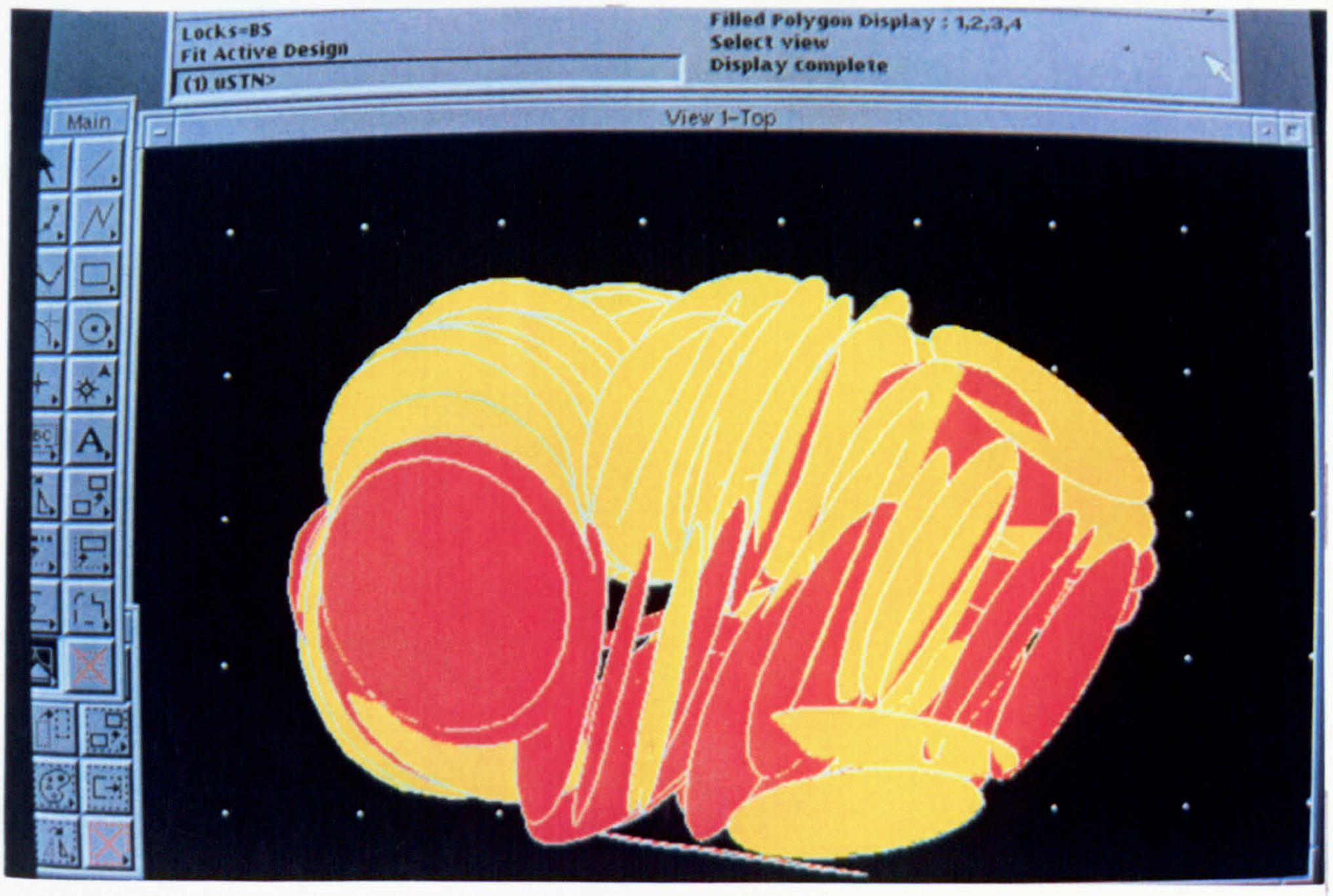
63



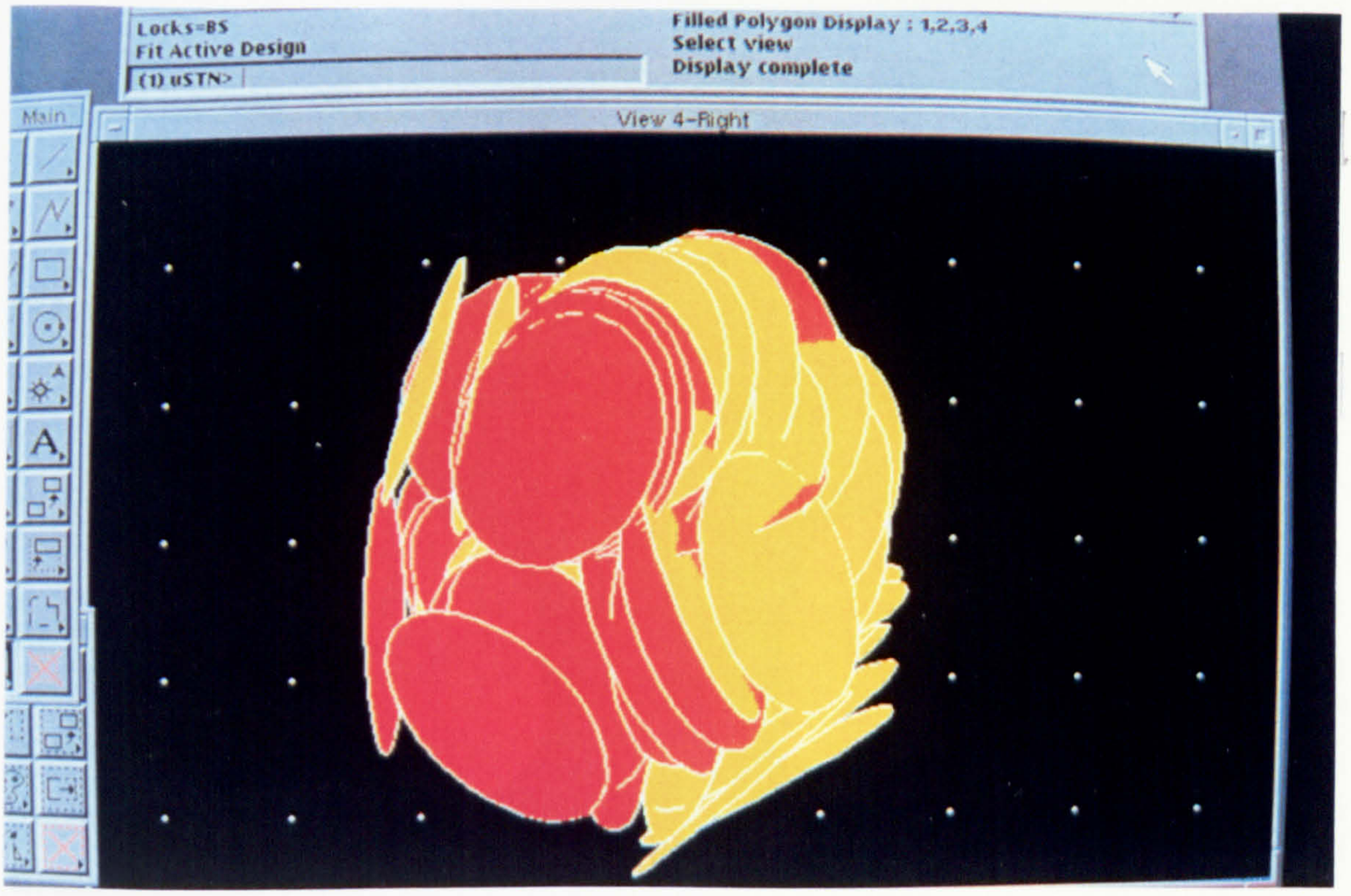
64


DOS
MSLINK
Coin.No.)
RICHBOROUGH HOARD COMPOSITIONS
Silver
Gold
Arsenic
Nickel
Lead
Tin
Zinc
Iron
Antimony
Chromium
Cobalt
View 1
Database
View
View
View

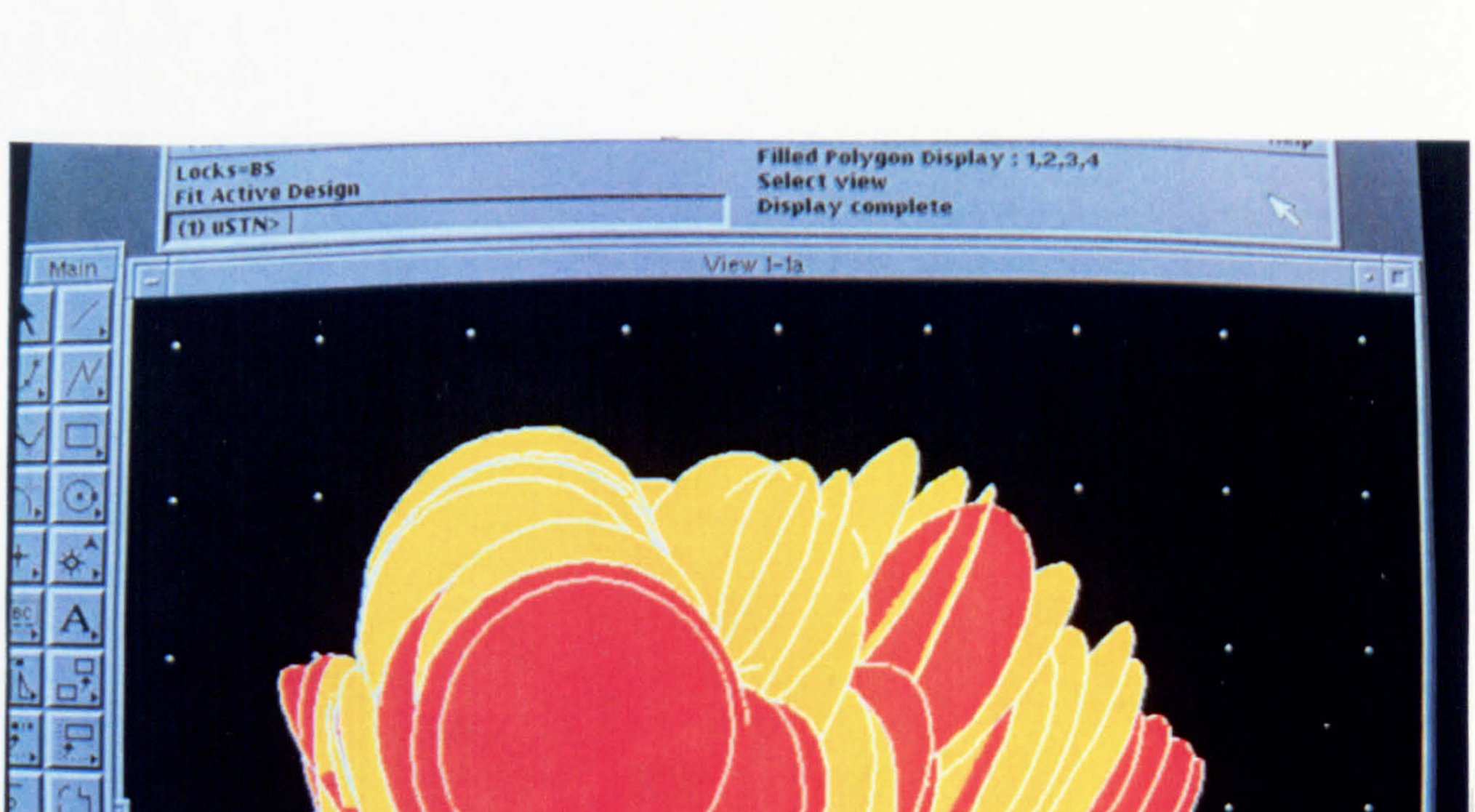
65


Locks=BS
Fit Active Design
(1) uSTN>
Filled Polygon Display : 1,2,3,4
Select view
Display complete
Main
View 1-Top

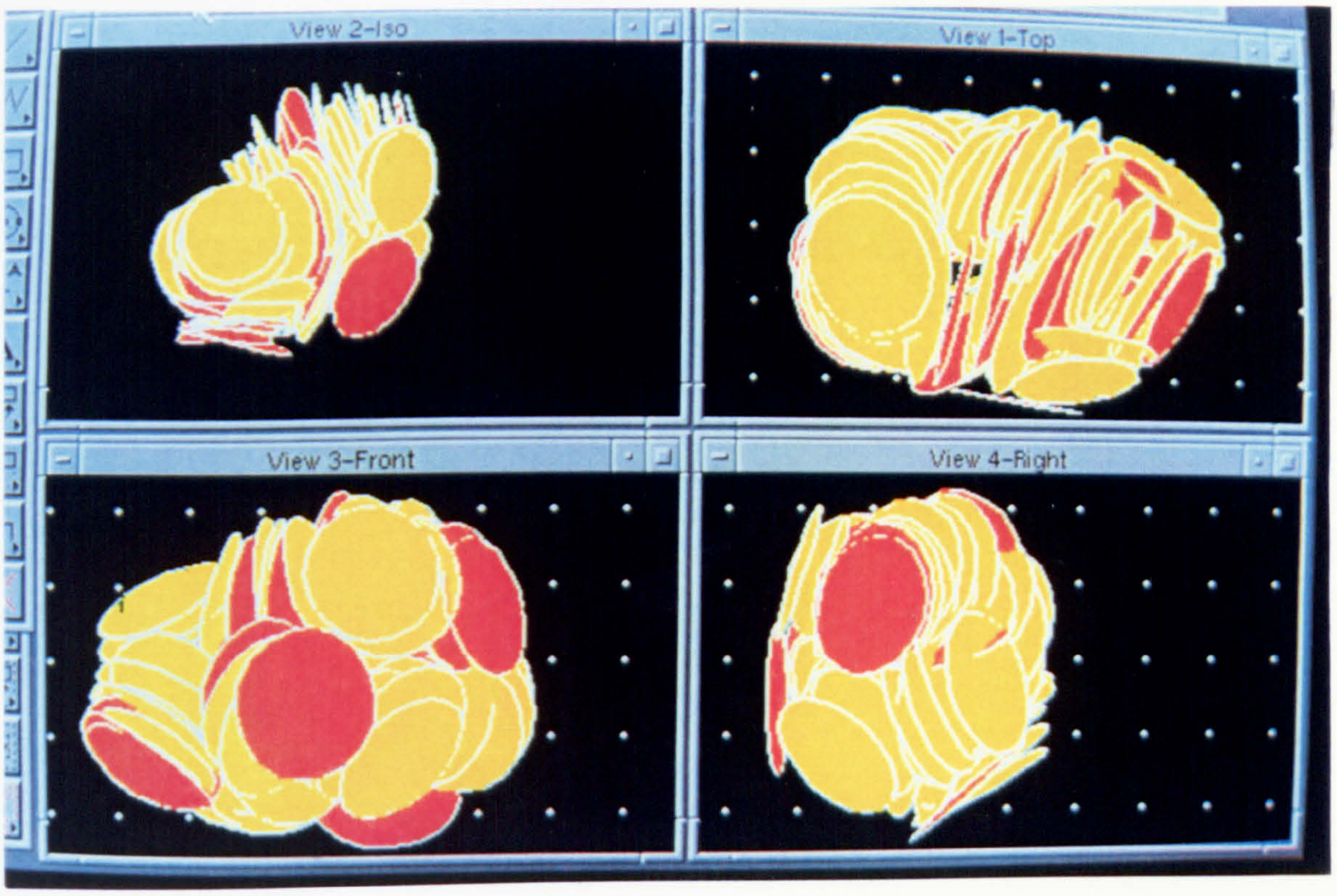
66


Locks=BS
Fit Active Design
(1) uSTN>
Filled Polygon Display : 1,2,3,4
Select view
Display complete
Main
View 4-Right

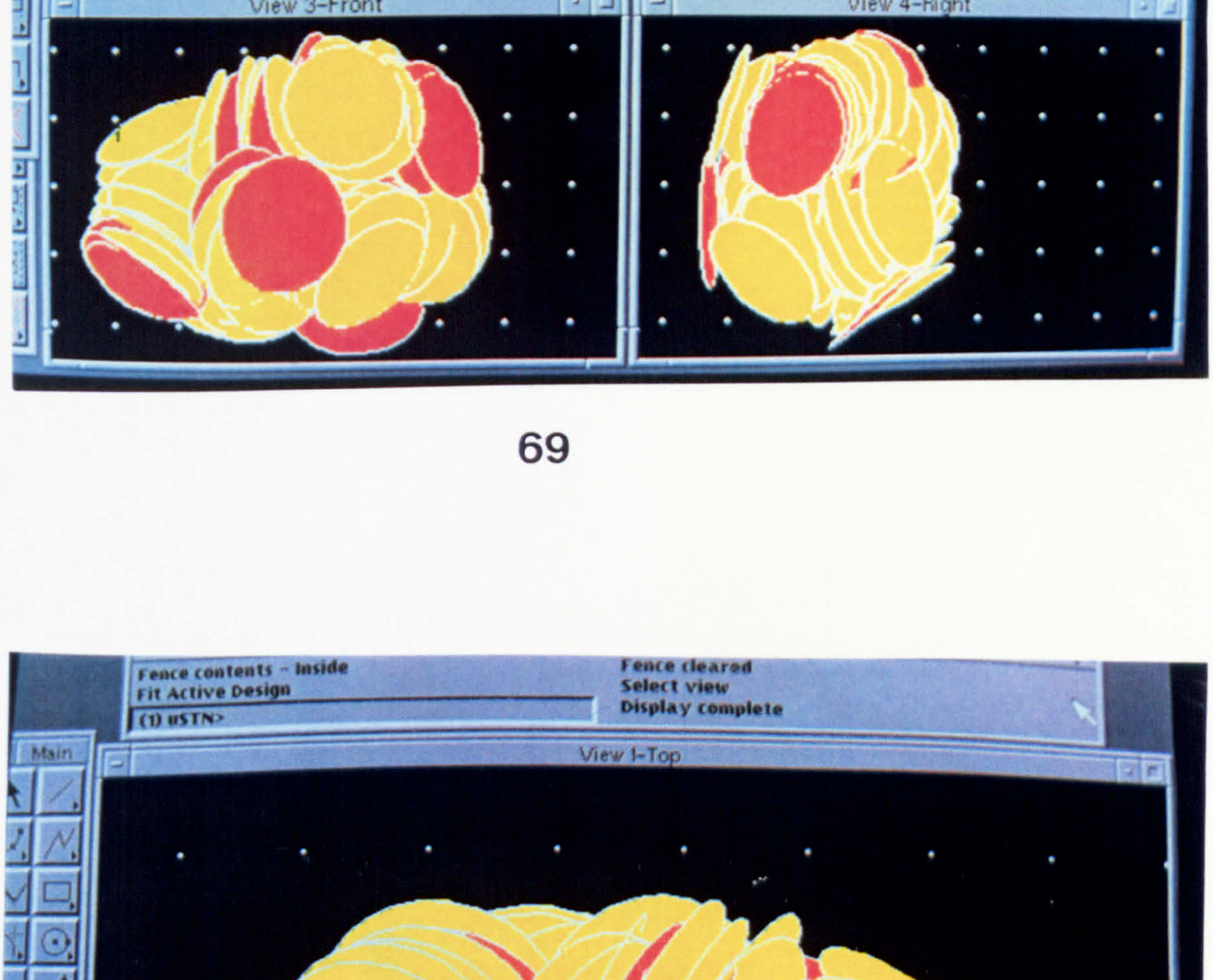
67


Locks=BS
Fit Active Design
(1) uSTN>
Filled Polygon Display : 1,2,3,4
Select view
Display complete
Main
View 1-1a

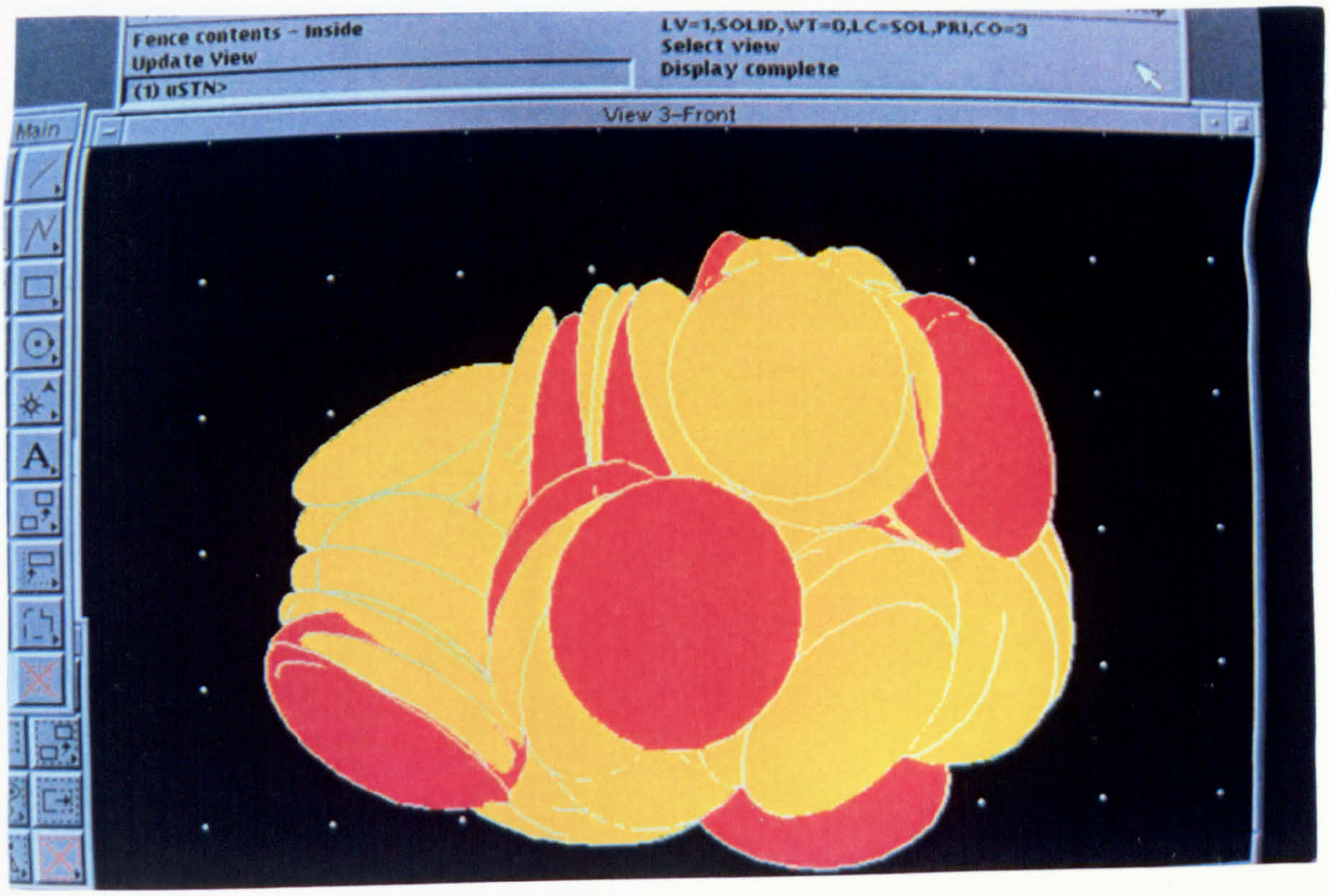
68


View 2-Iso
View 1-Top
View 3-Front
View 4-Right

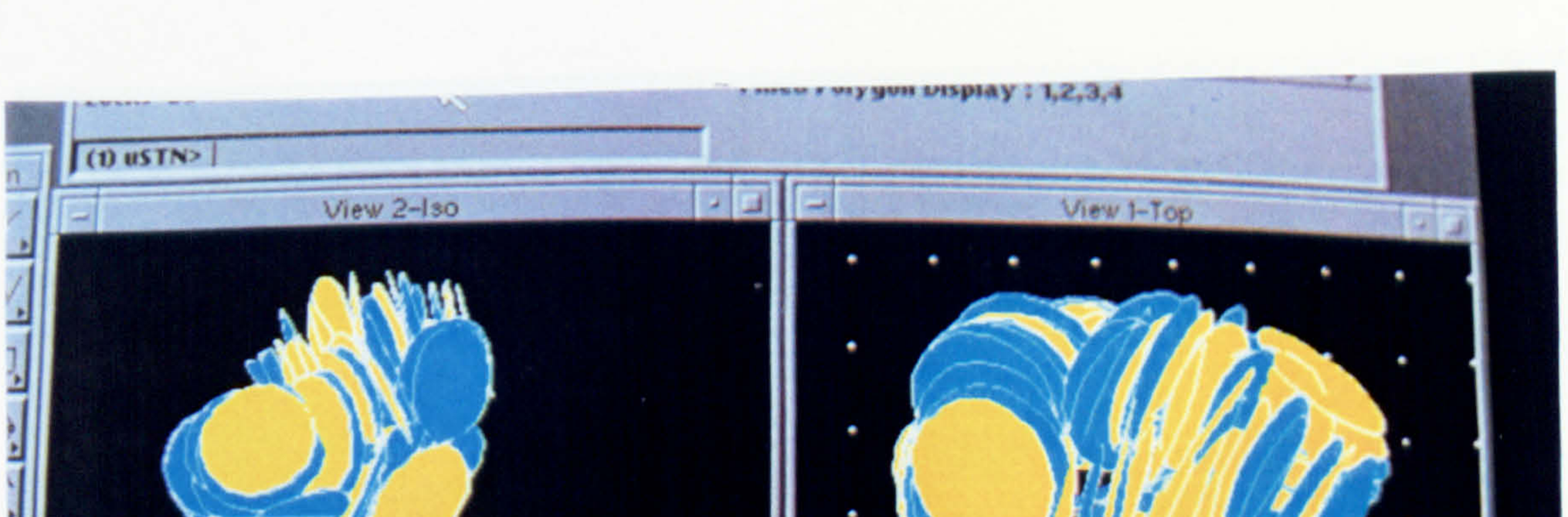
69


Fence contents - Inside
Fit Active Design
(1) uSTN>
Fence cleared
Select view
Display complete
Main
View 1-Top

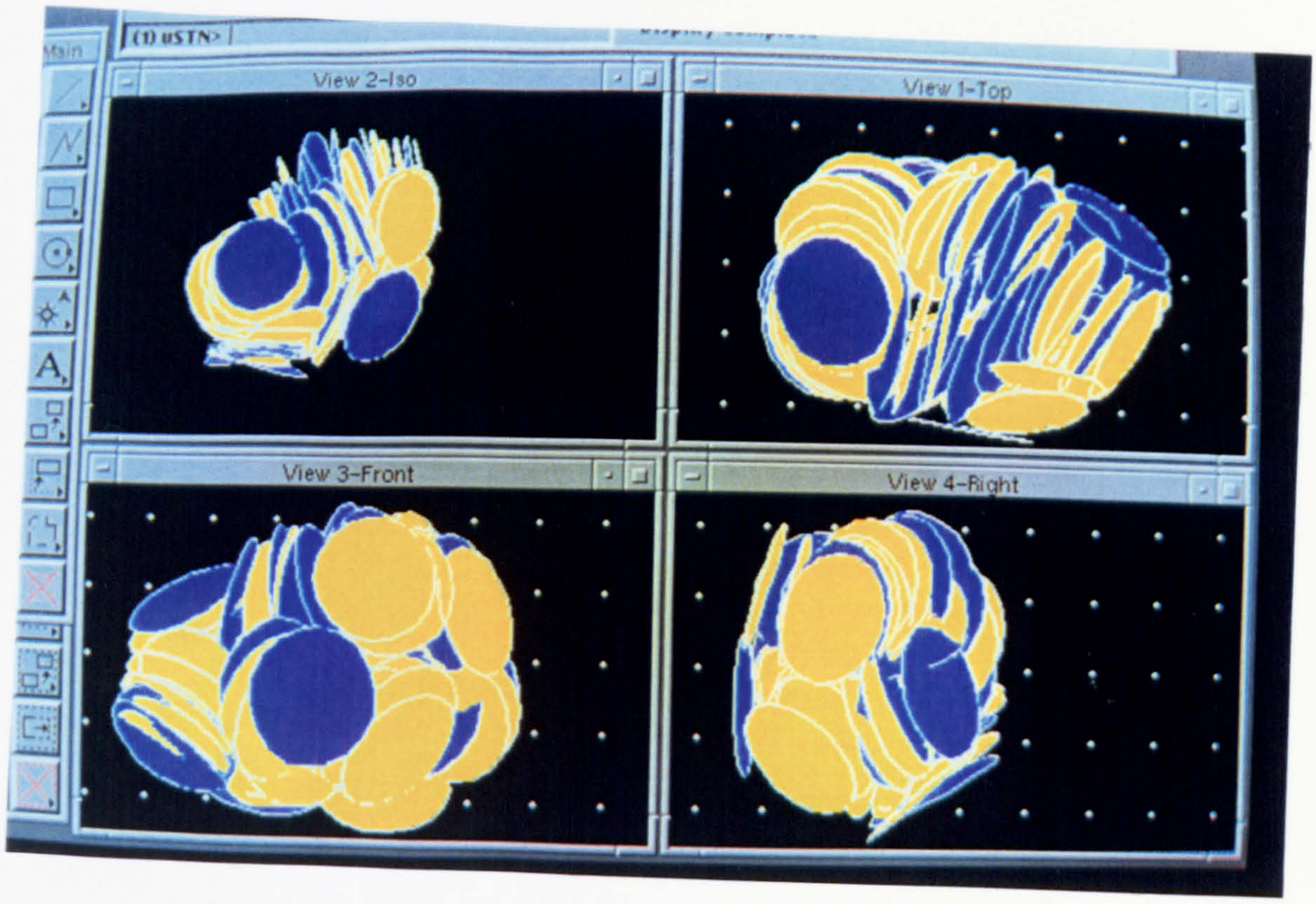
70


Fence contents - Inside
Update View
(1) uSTN>
LV=1,SOLID,WT=0,LC=SOL,PRI,CO=3
Select view
Display complete
View 3-Front
Main

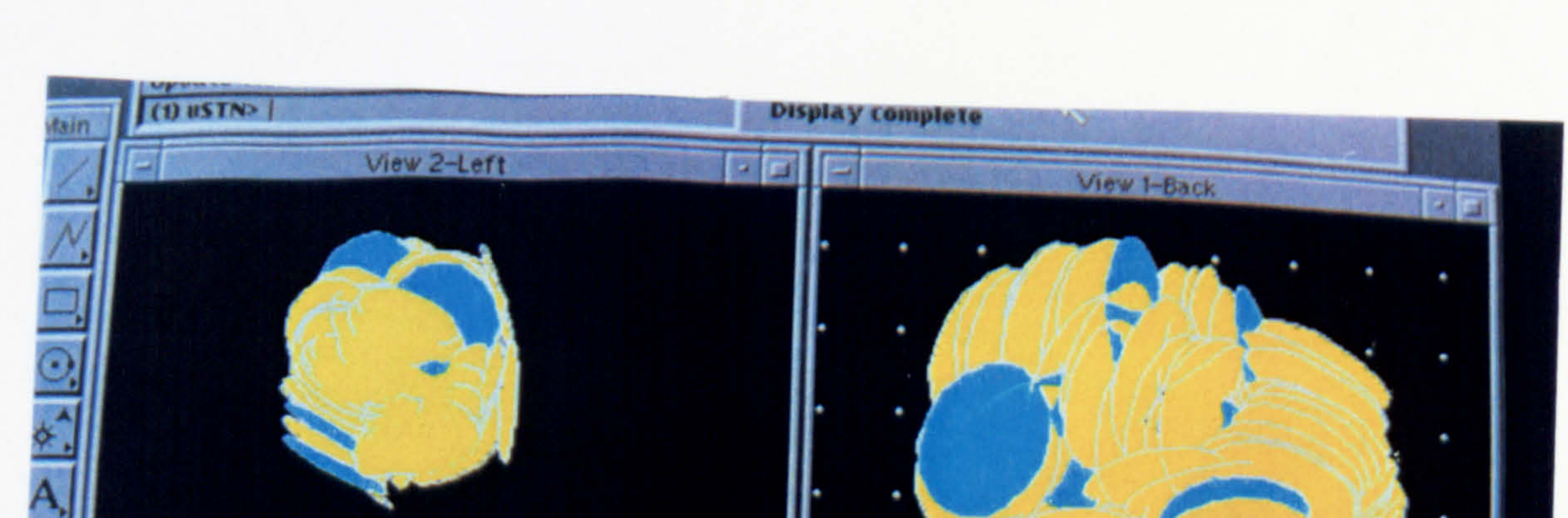
71


(1) uSTN>
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

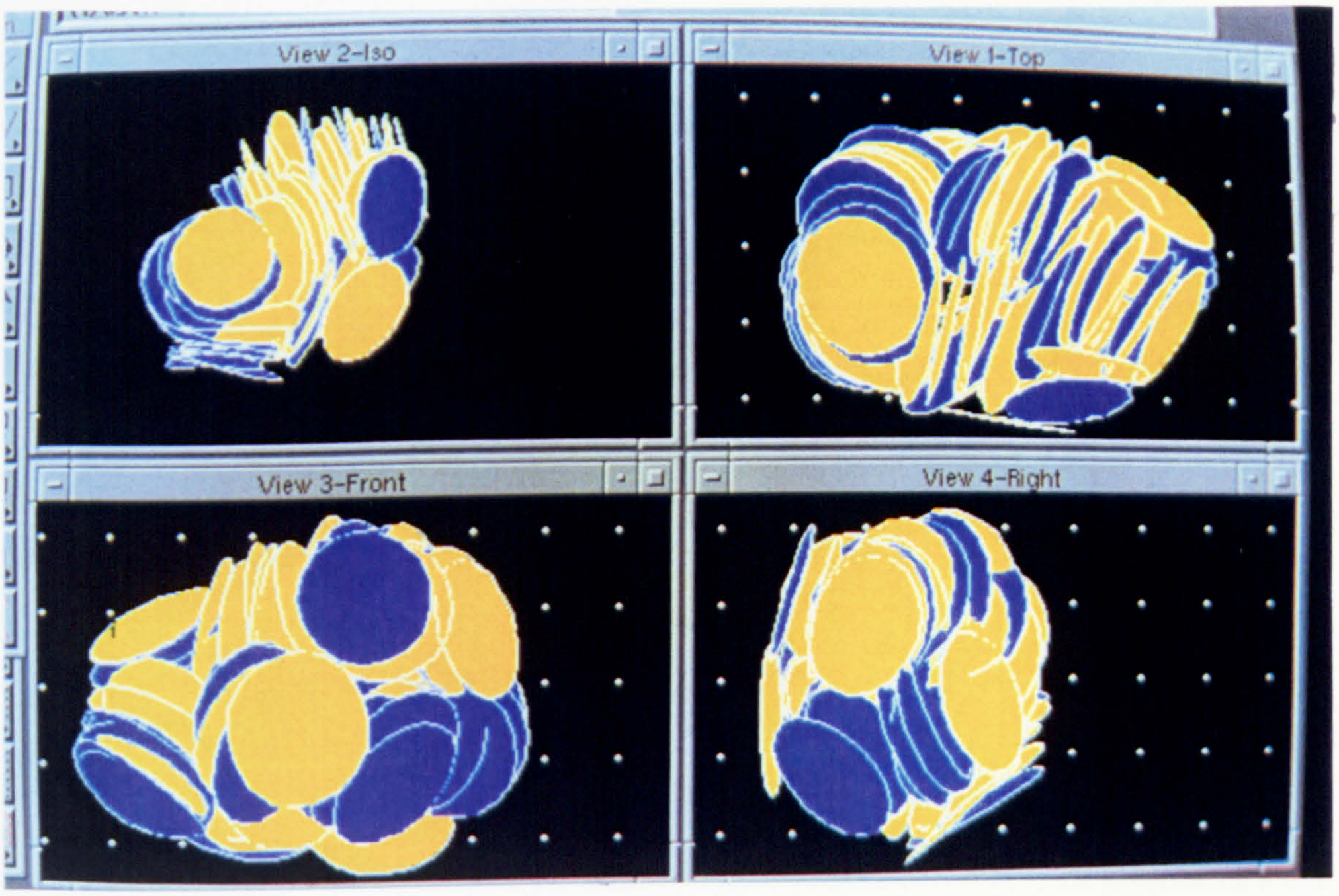
72


(1) uSTN>
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

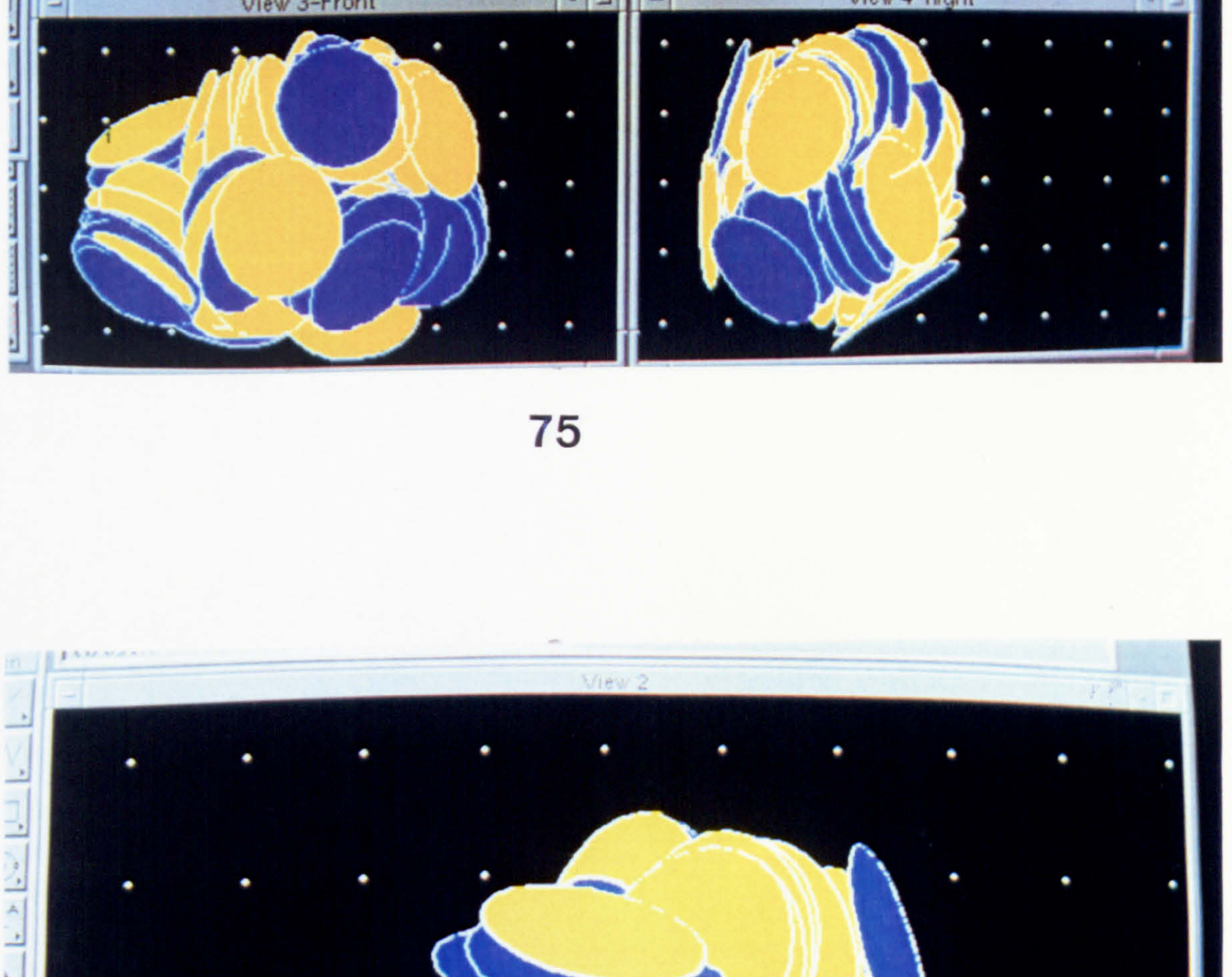
73


(1) uSTN>
Display complete
View 2-Left
View 1-Back
View 3-Front
View 4-Right

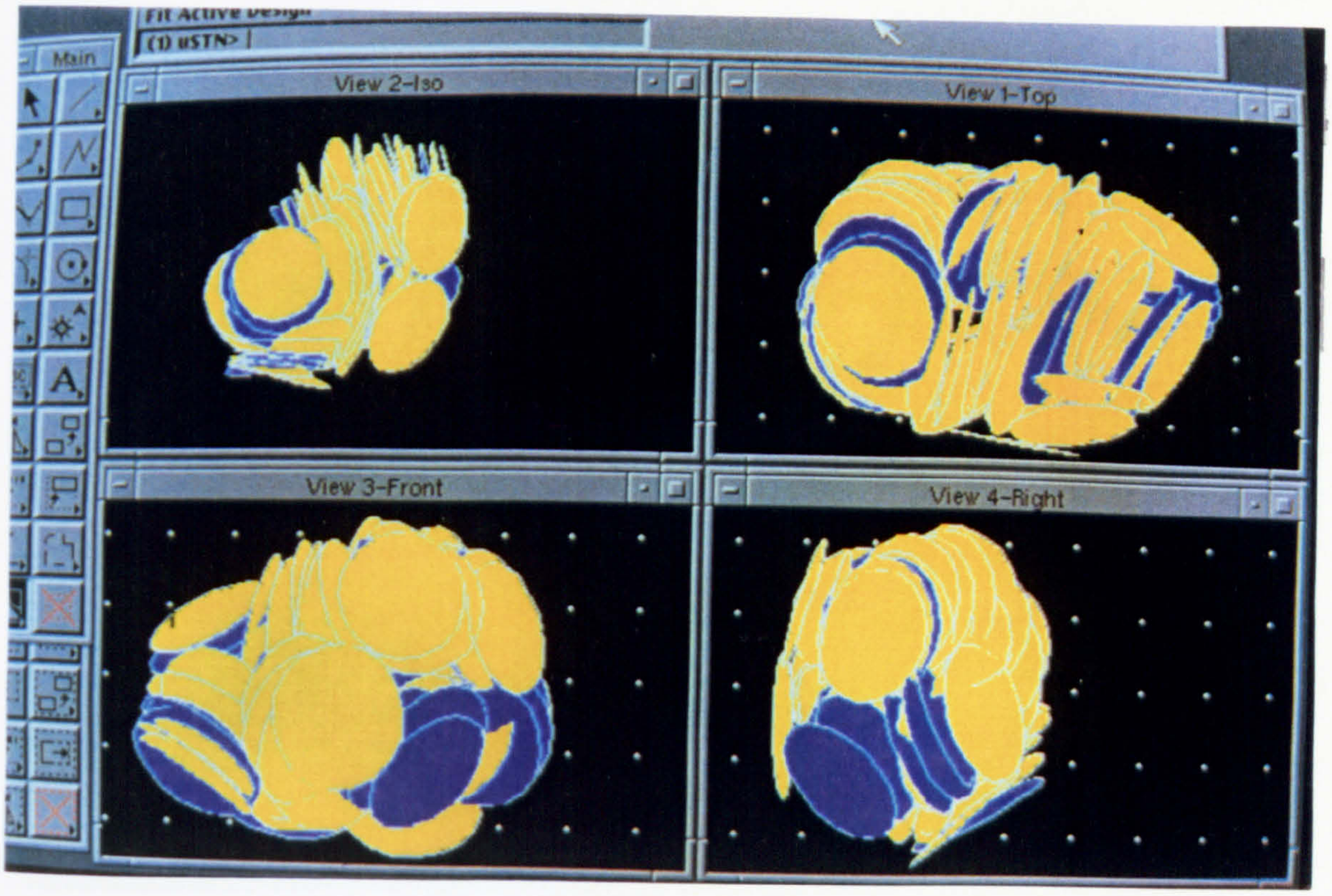
74



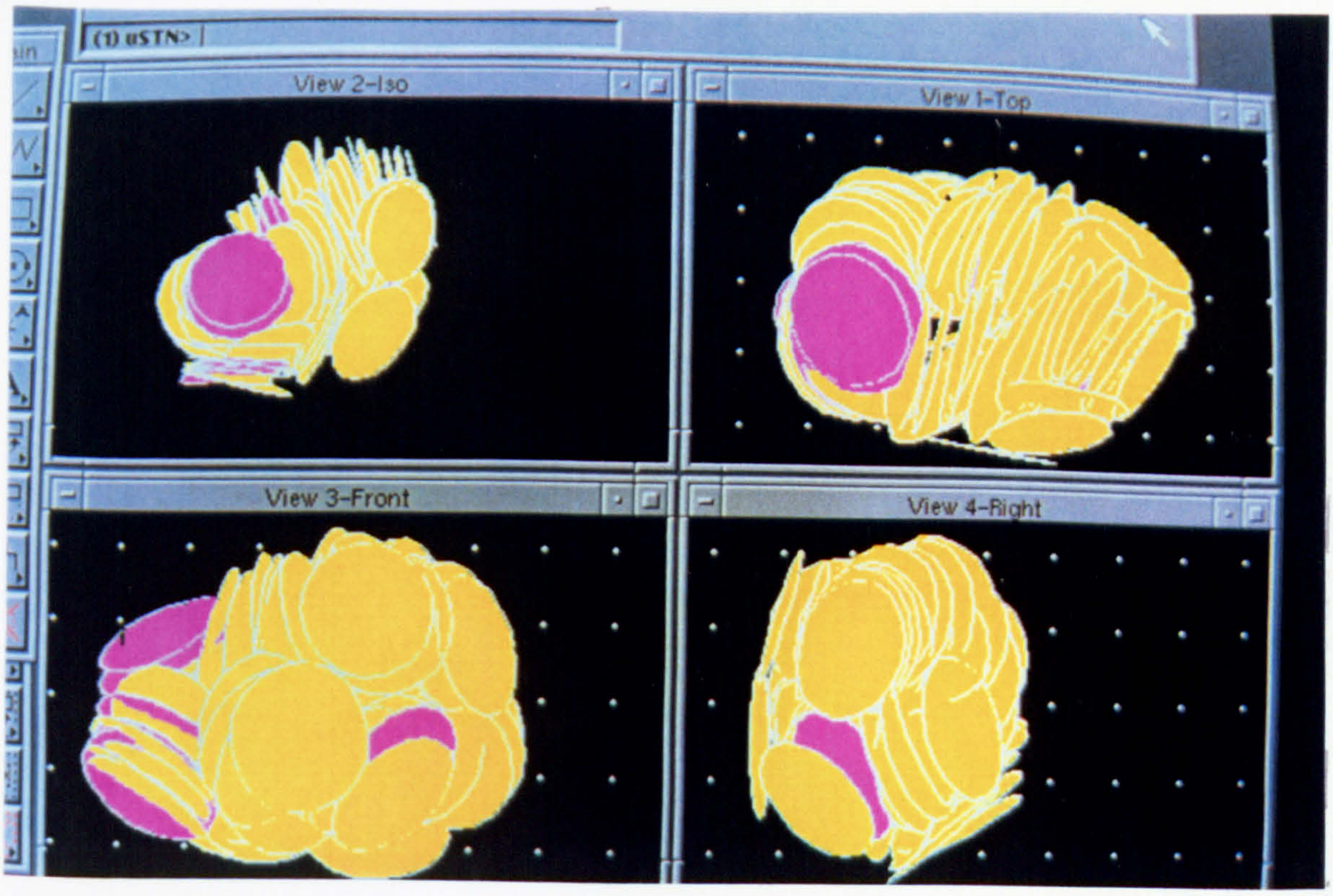
75



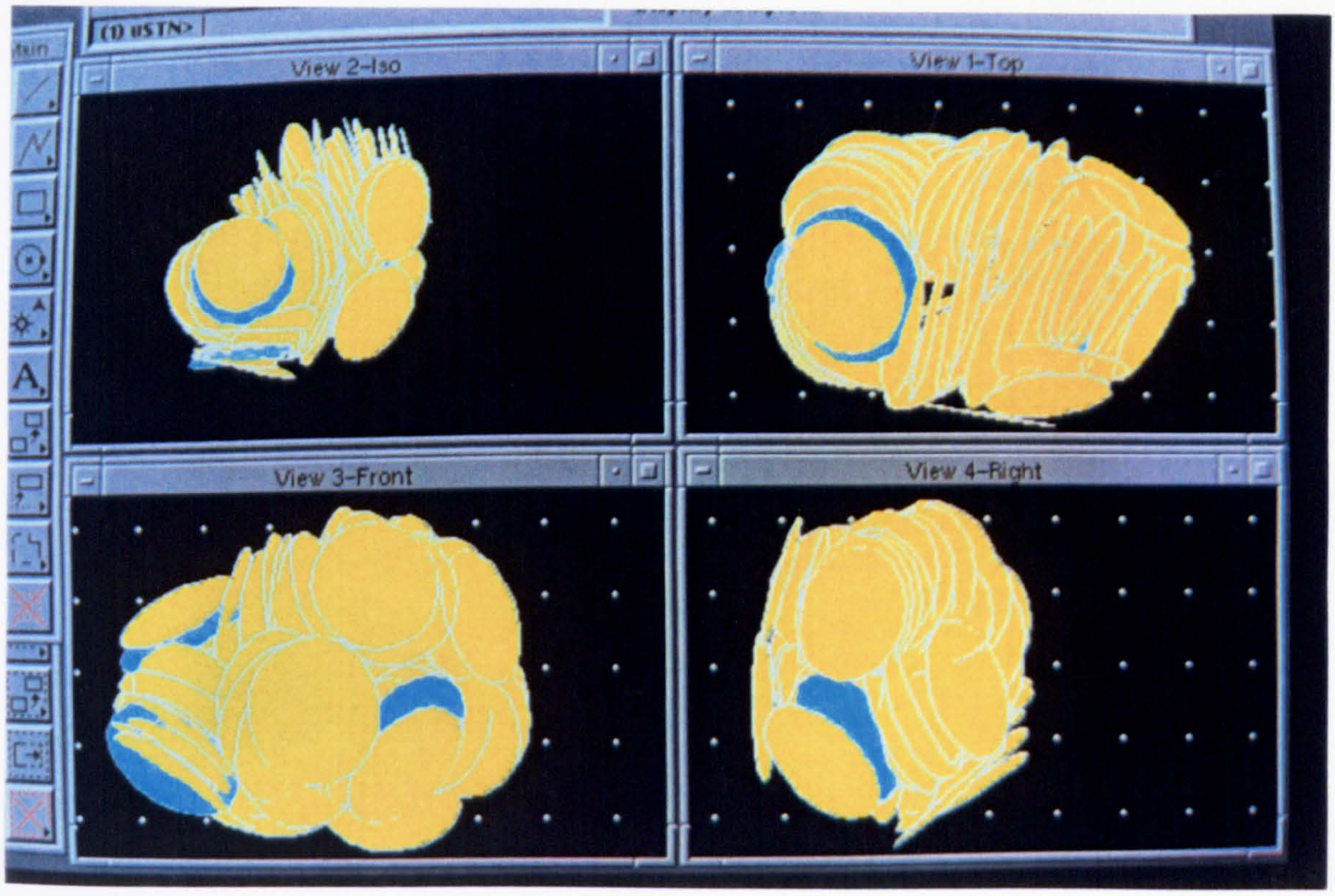
76


Main
(1) uSTN>
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

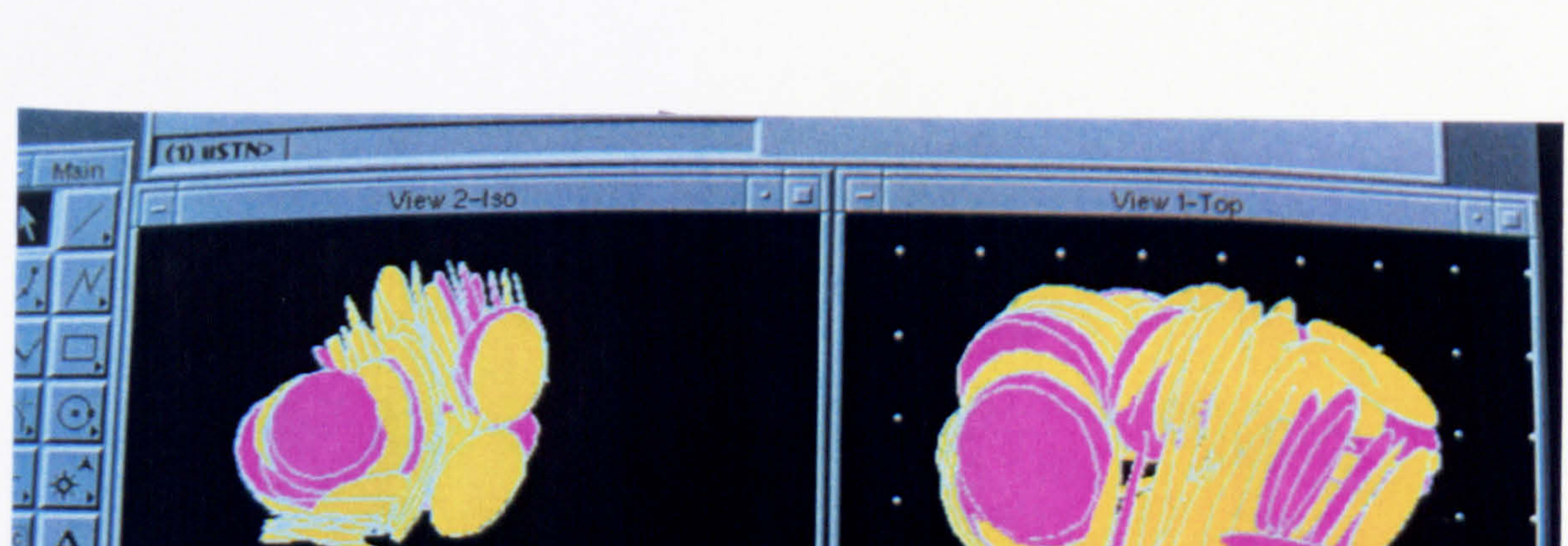
77


(1) uSTN>
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

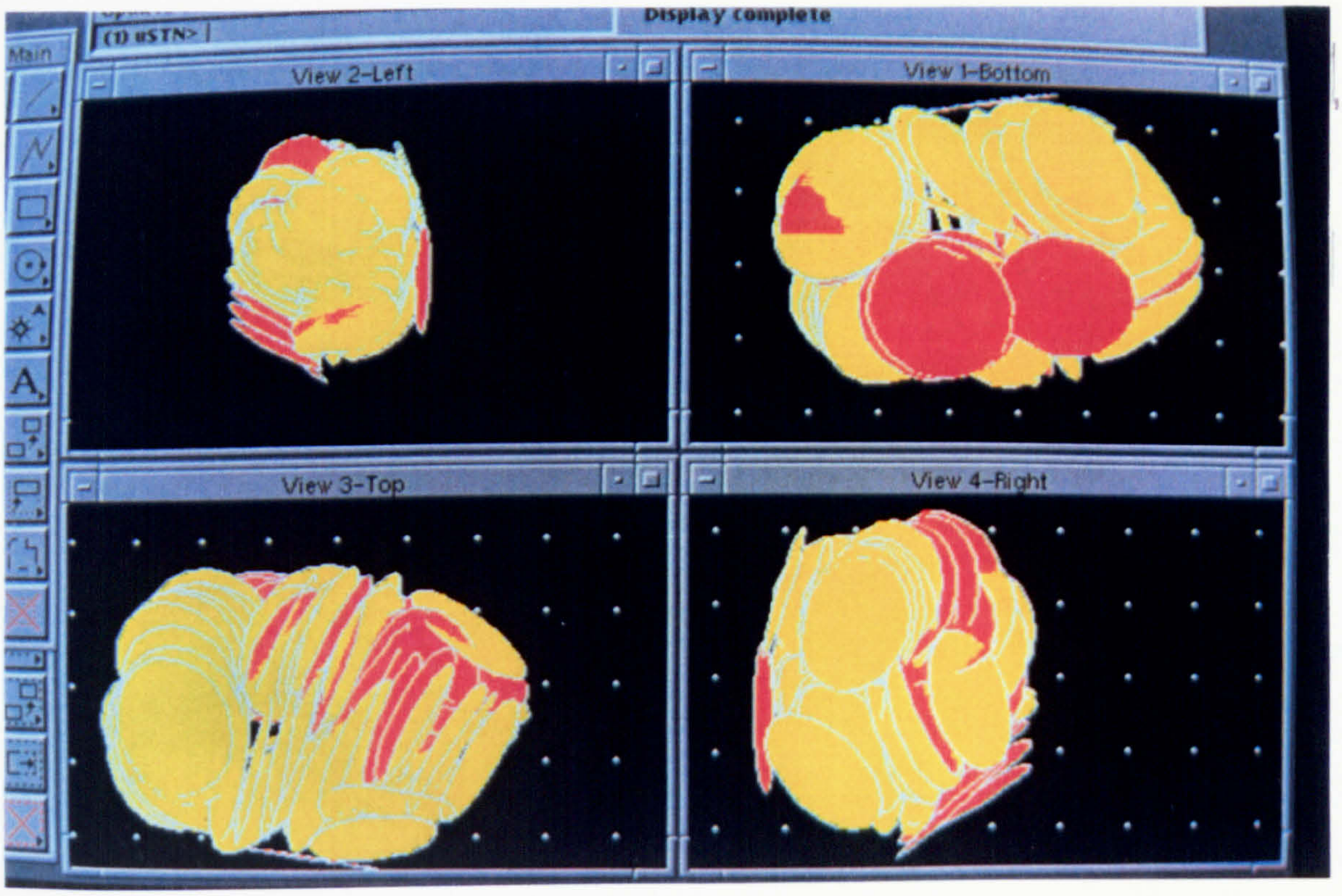
78


(1) MSTN>
Main
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

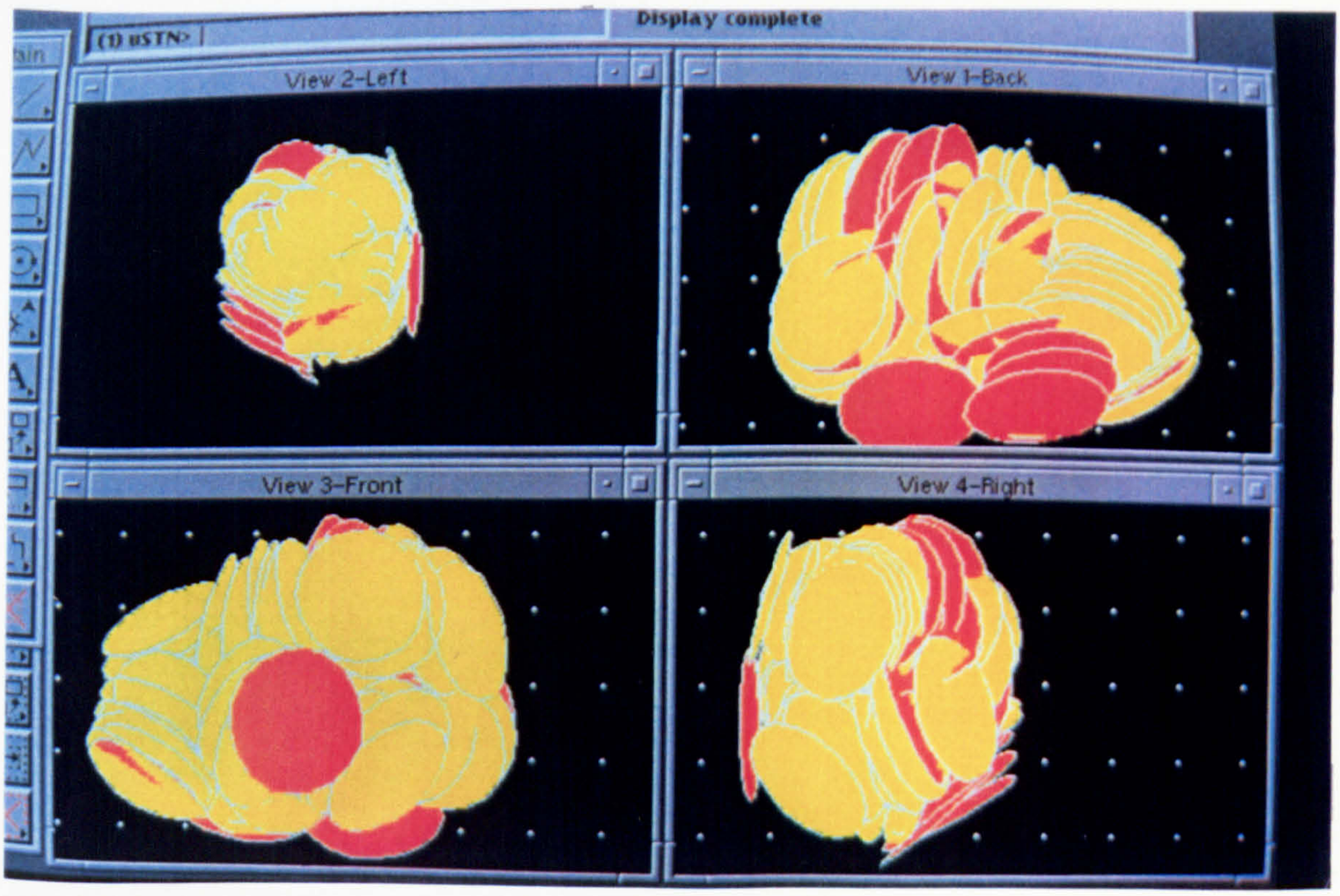
79


(1) MSTN>
Main
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

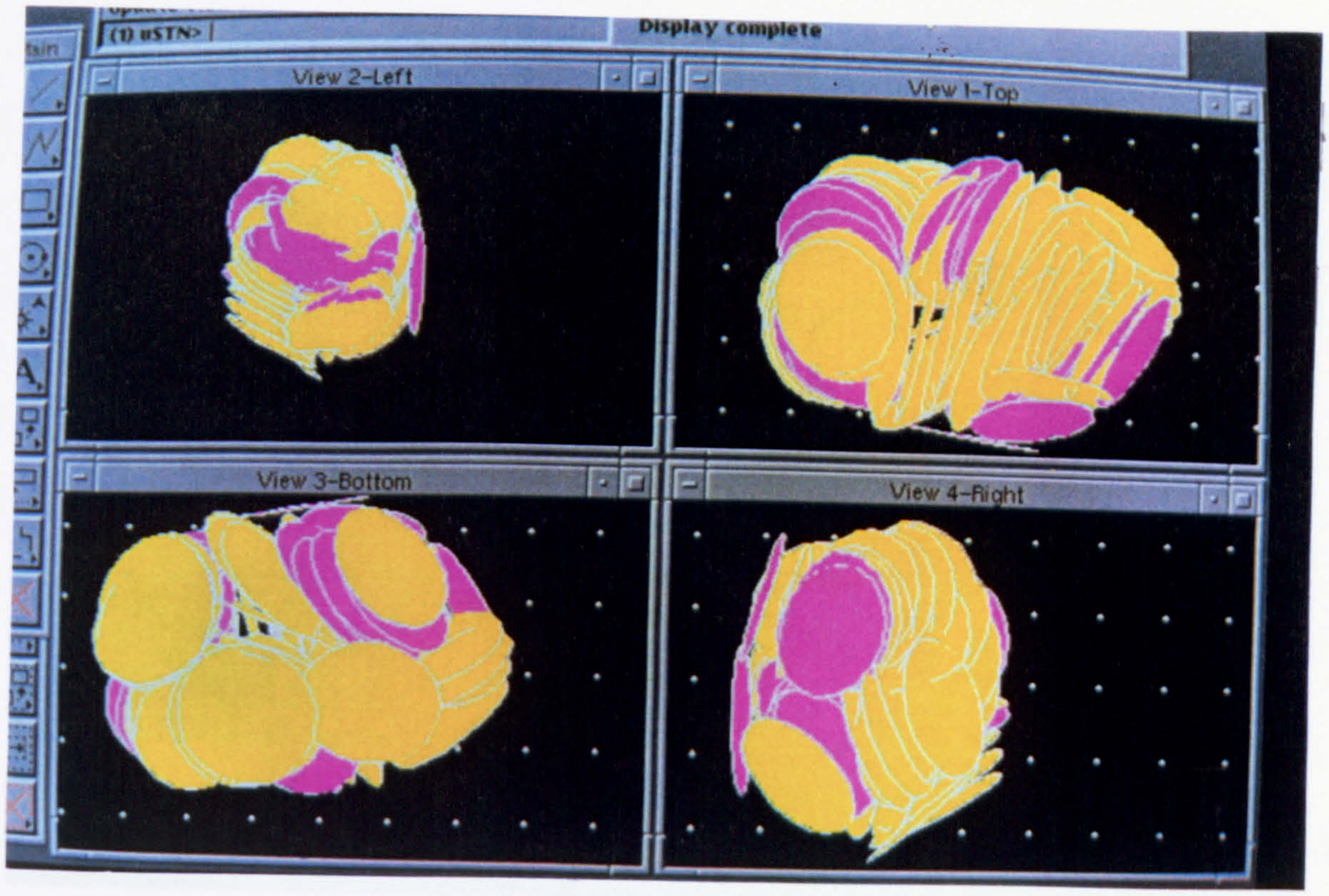
80


Display complete
(1) uSTN>
Main
View 2-Left
View 1-Bottom
View 3-Top
View 4-Right

81


Display complete
(1) uSTN>
View 2-Left
View 1-Back
View 3-Front
View 4-Right

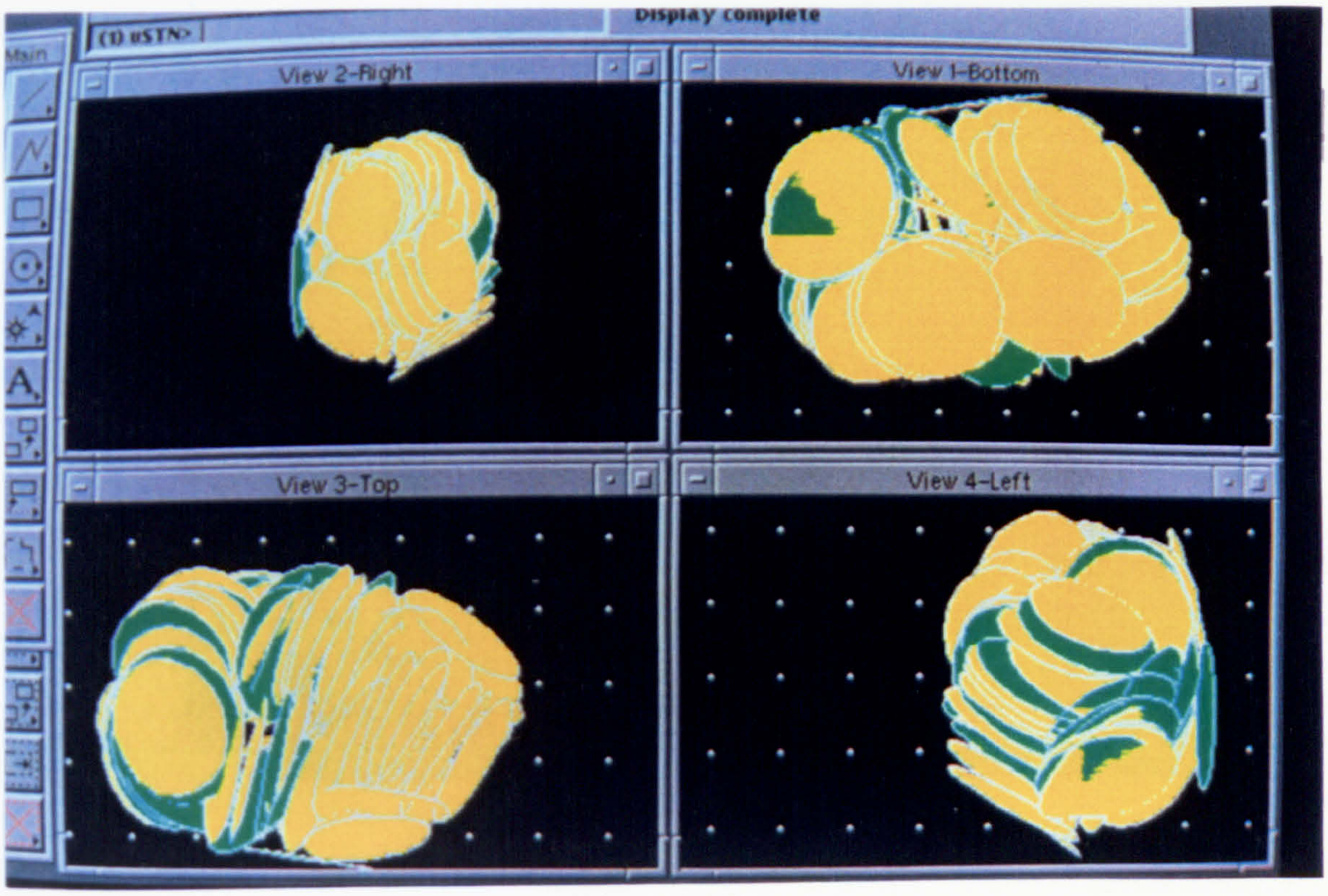
82


(1) uSTN>
Display complete
View 2-Left
View 1-Top
View 3-Bottom
View 4-Right

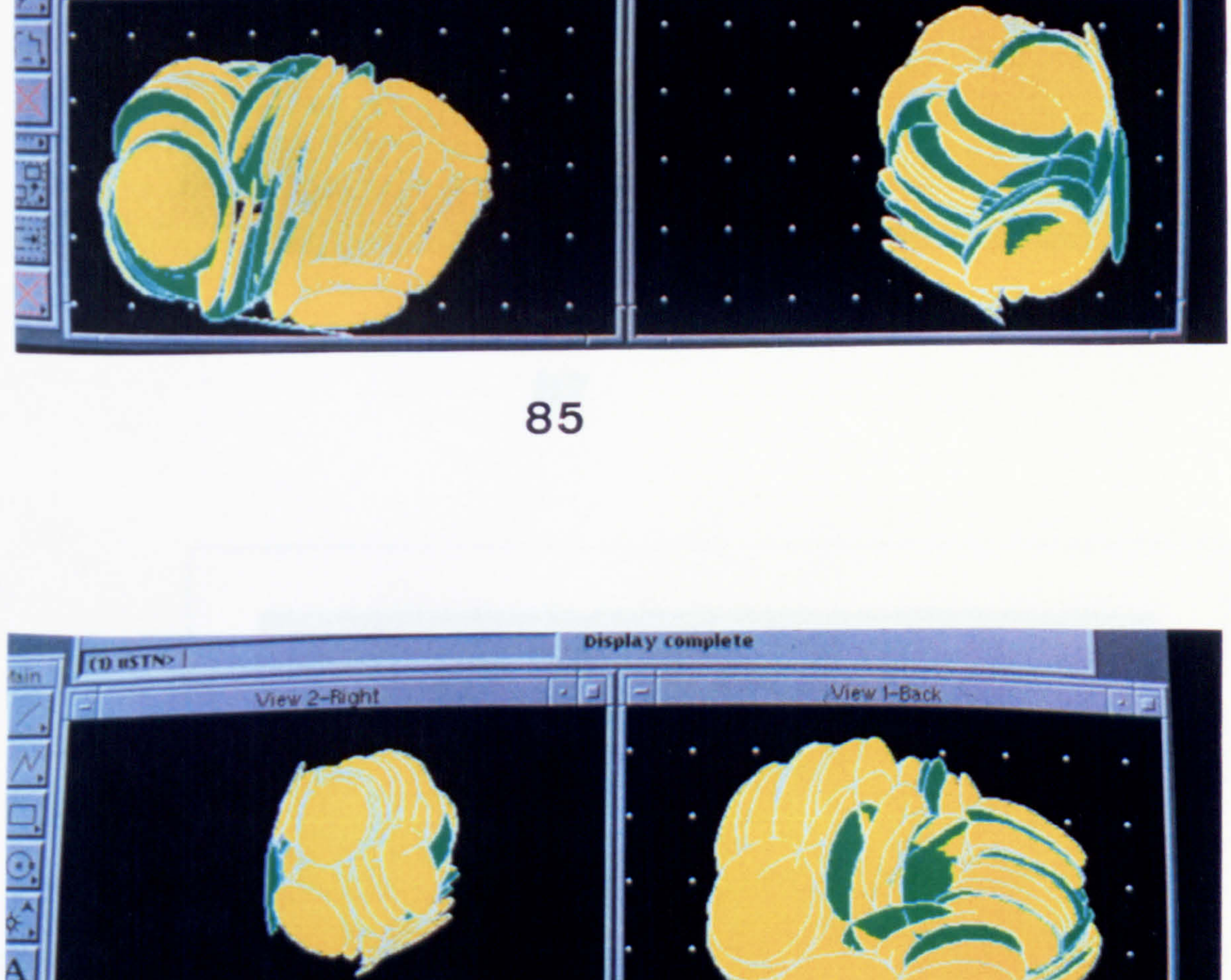
83


(1) uSTN>
View 2-Iso
View 1-Top
View 3-Front
View 4-Right

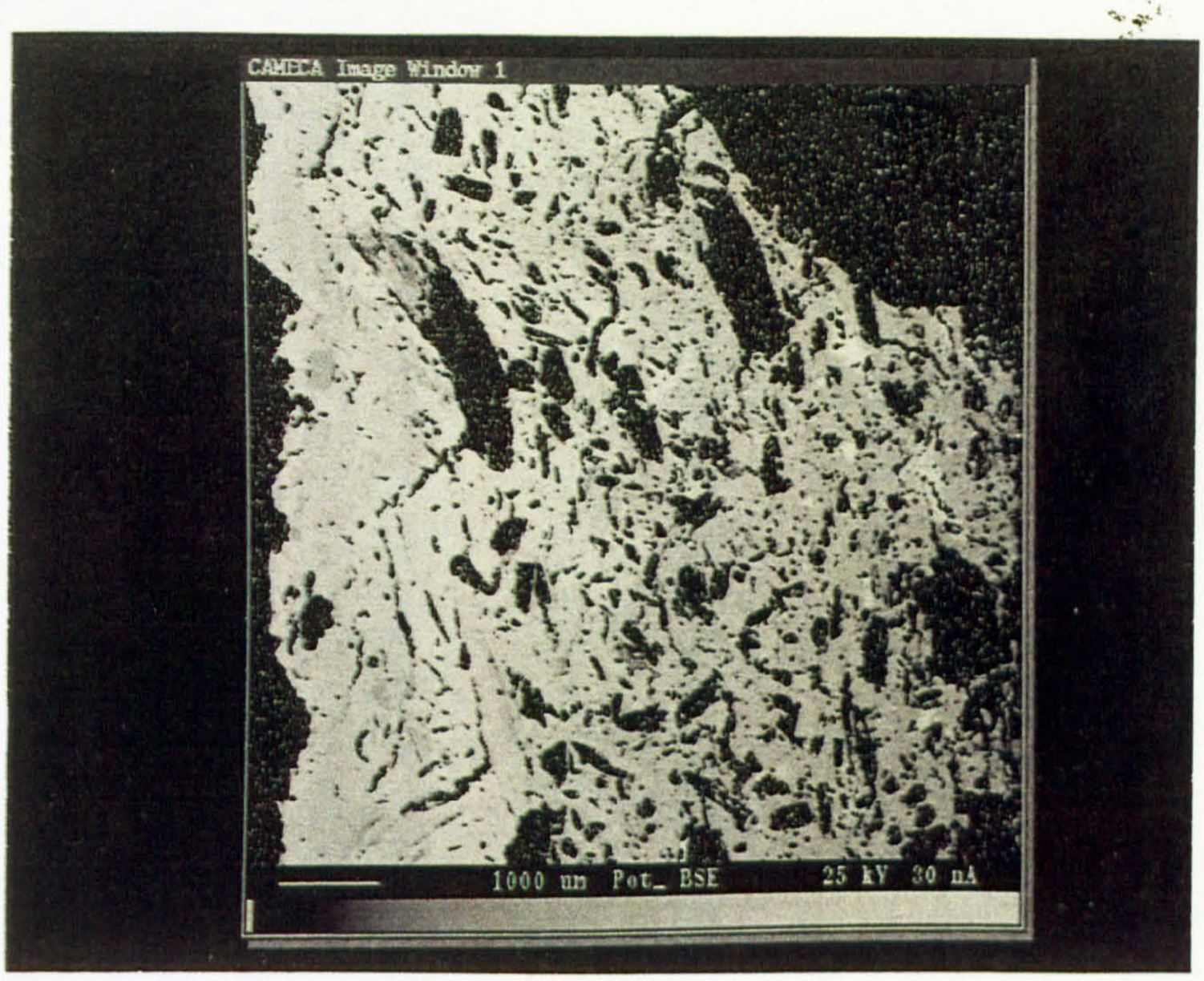
84


Display complete
(D) uSTN>
Main
View 2-Right
View 1-Bottom
View 3-Top
View 4-Left

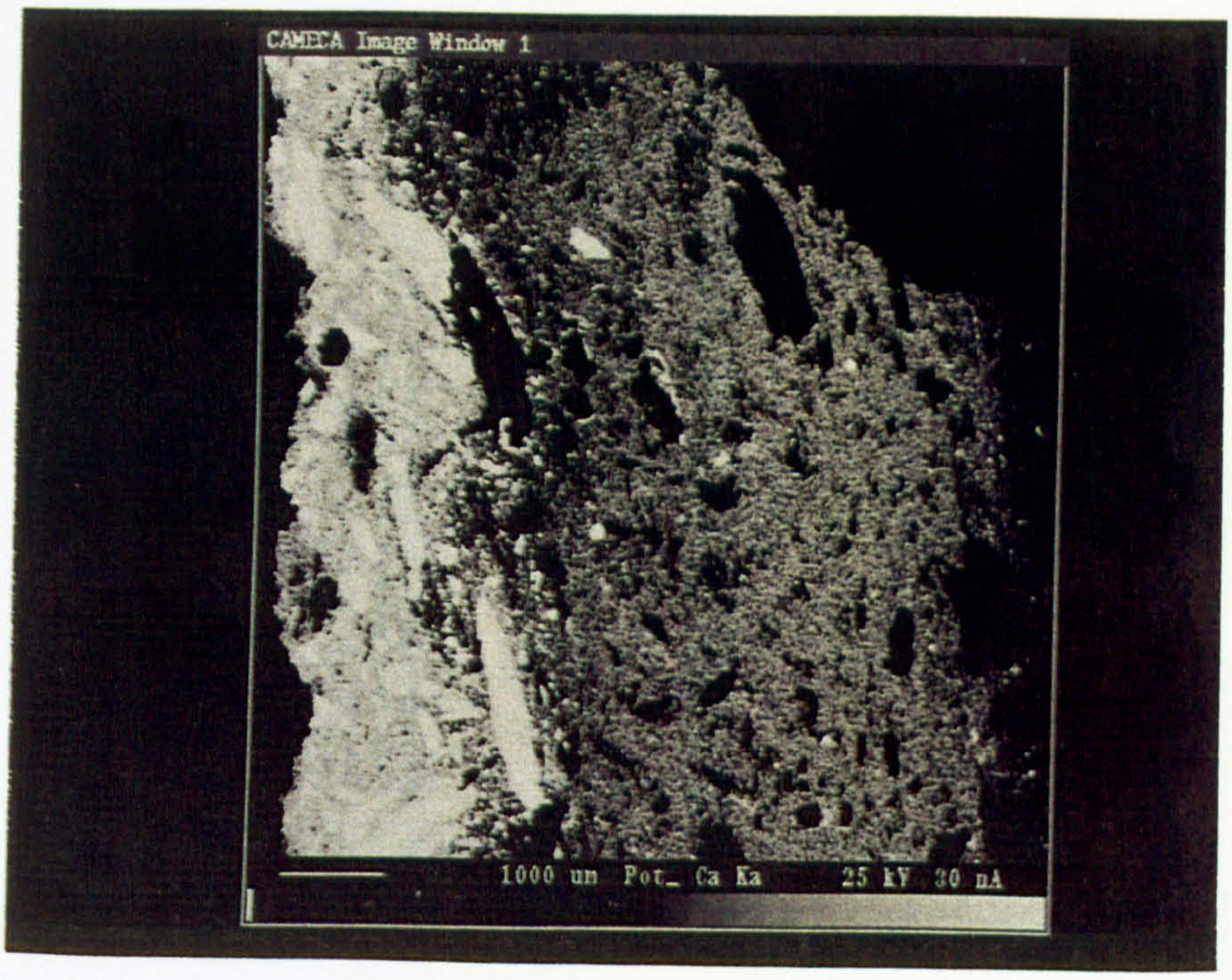
85


Display complete
(D) uSTN>
Main
View 2-Right
View 1-Back
View 3-Front
View 4-Left

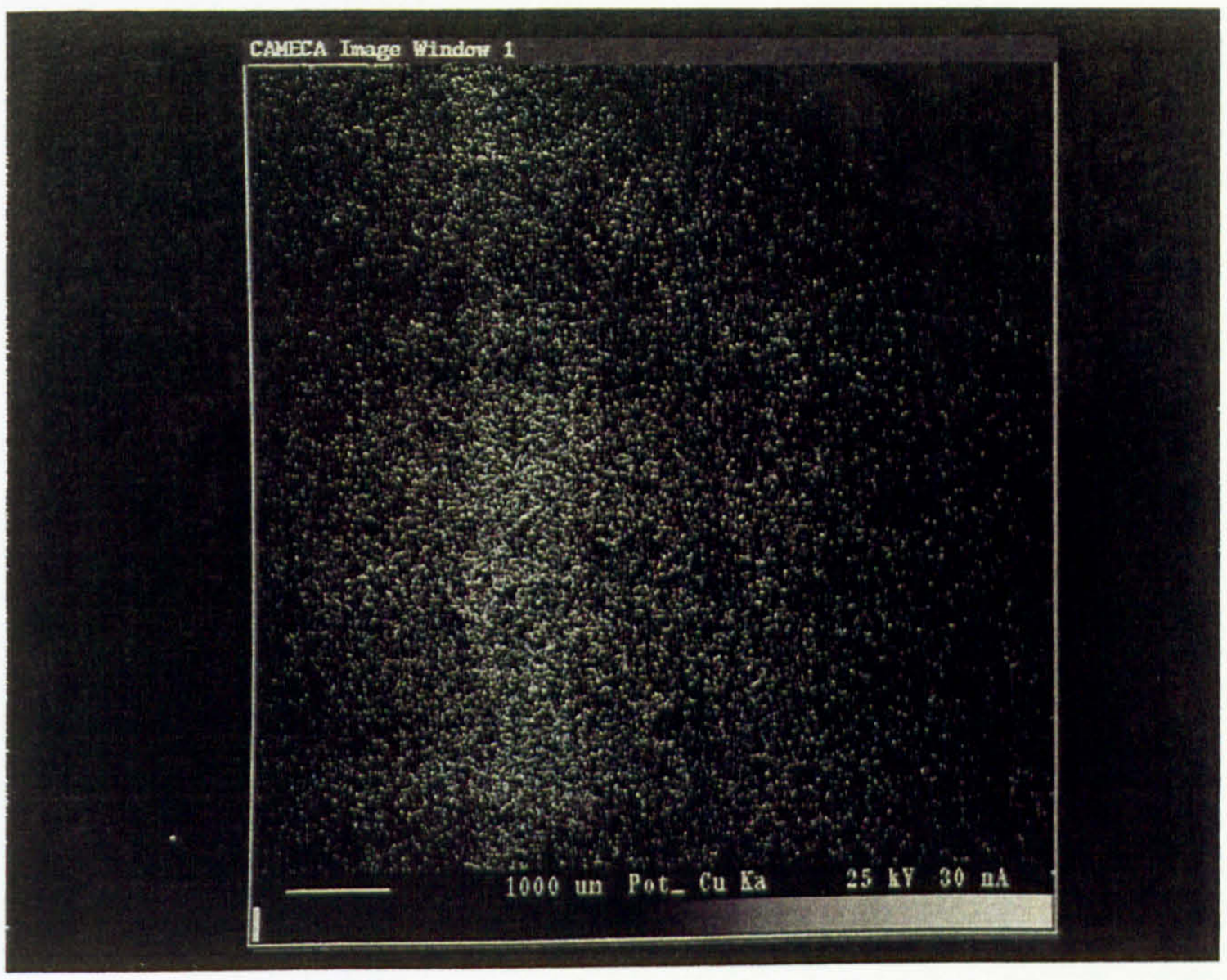
86


CAMECA Image Window 1
1000 um Pot_ BSE
25 kV 30 nA

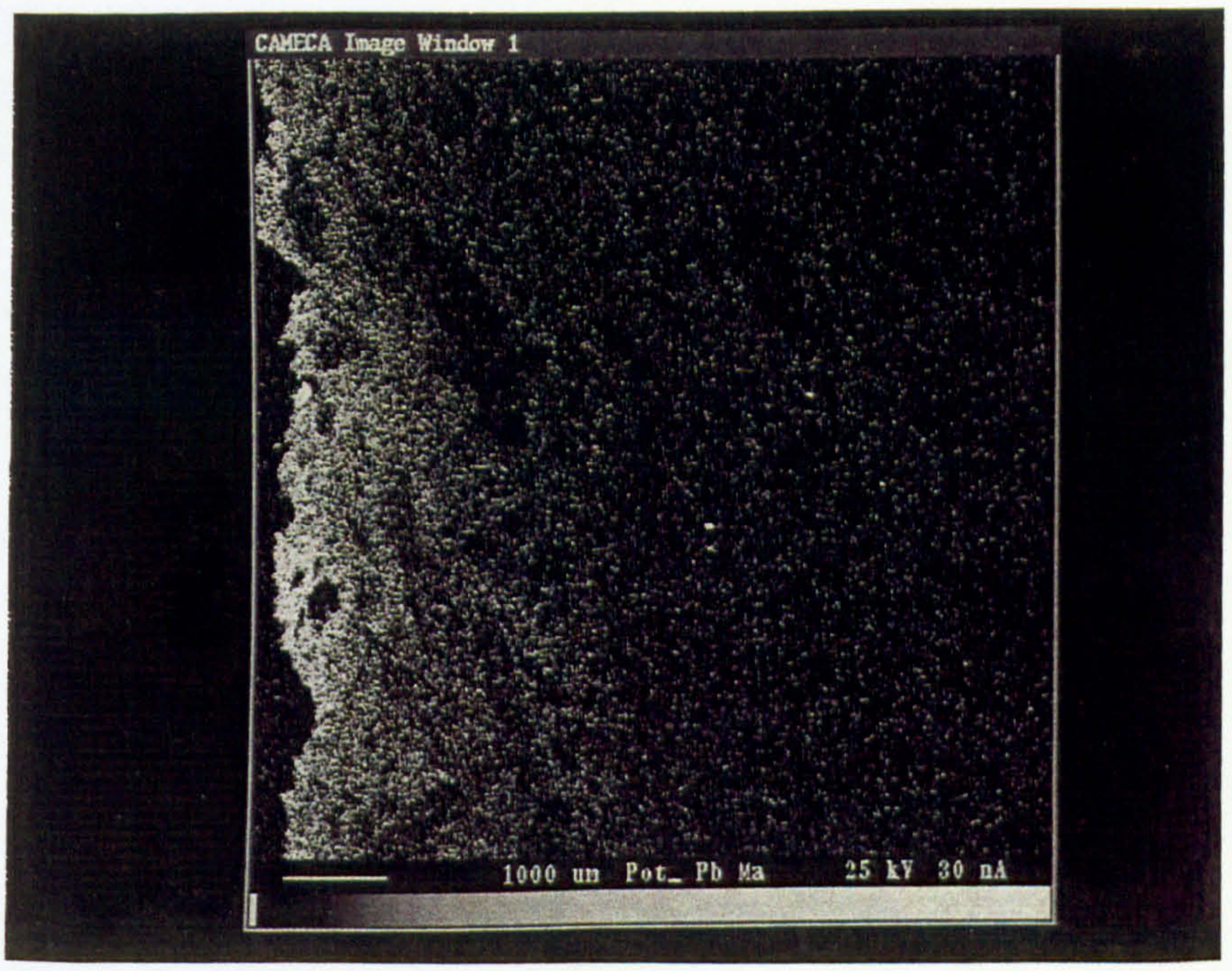
87


CAMECA Image Window 1
1000 um Pot_ Ca Ka
25 kV 30 nA

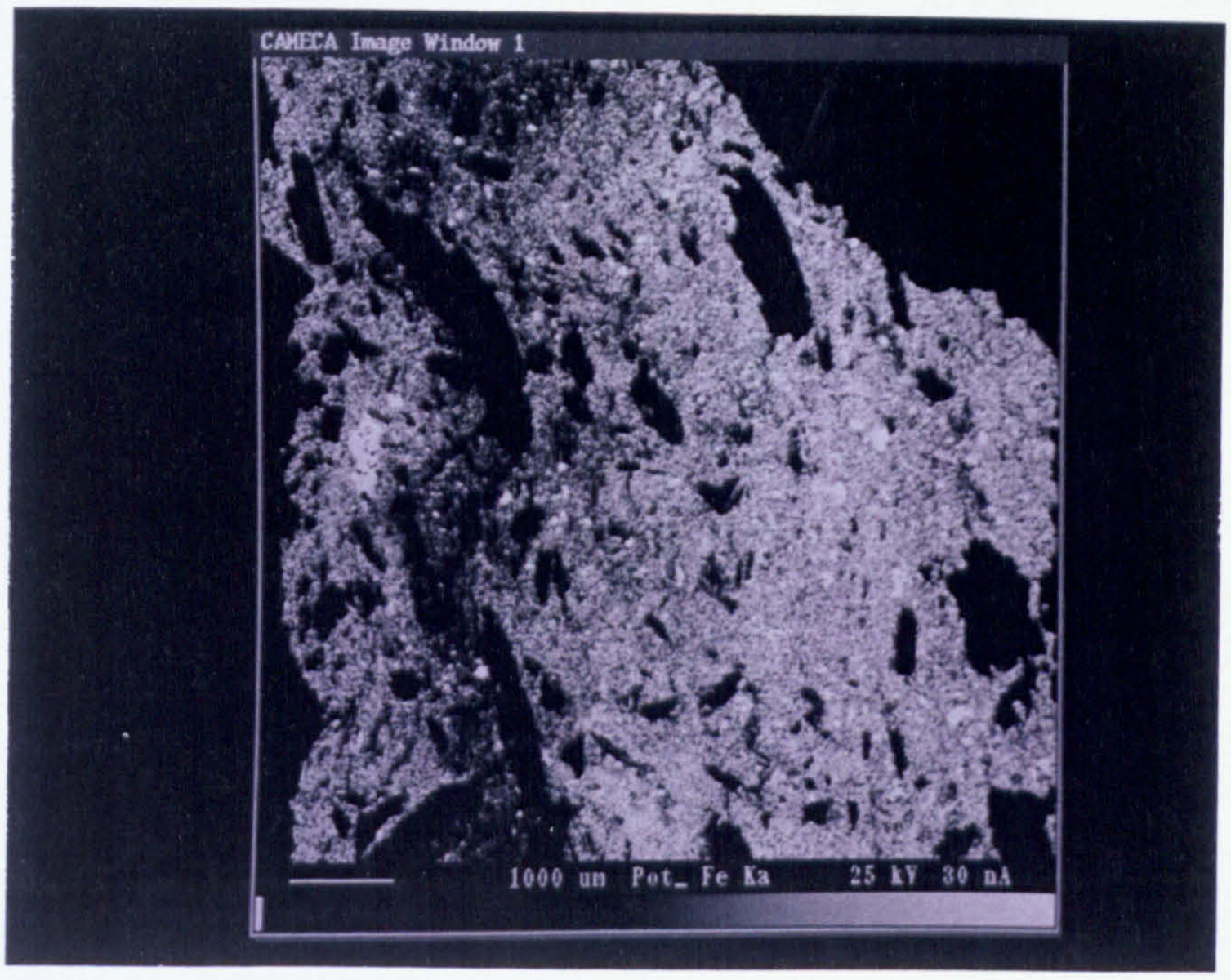
88


CAMECA Image Window 1
1000 um Pot_ Cu Ka 25 kV 30 nA

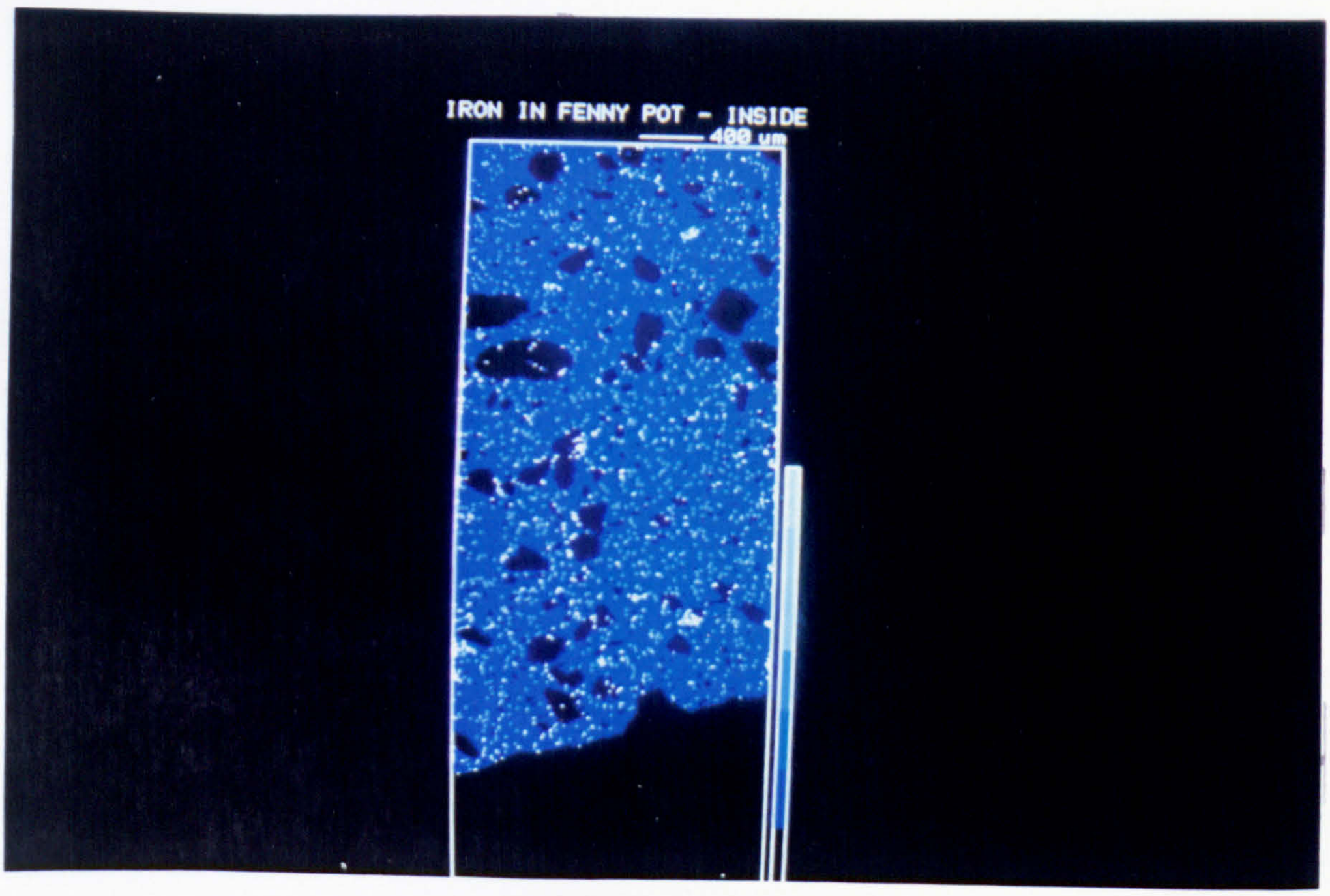
89


CAMECA Image Window 1
1000 um Pot_ Pb Ma 25 kV 30 nA

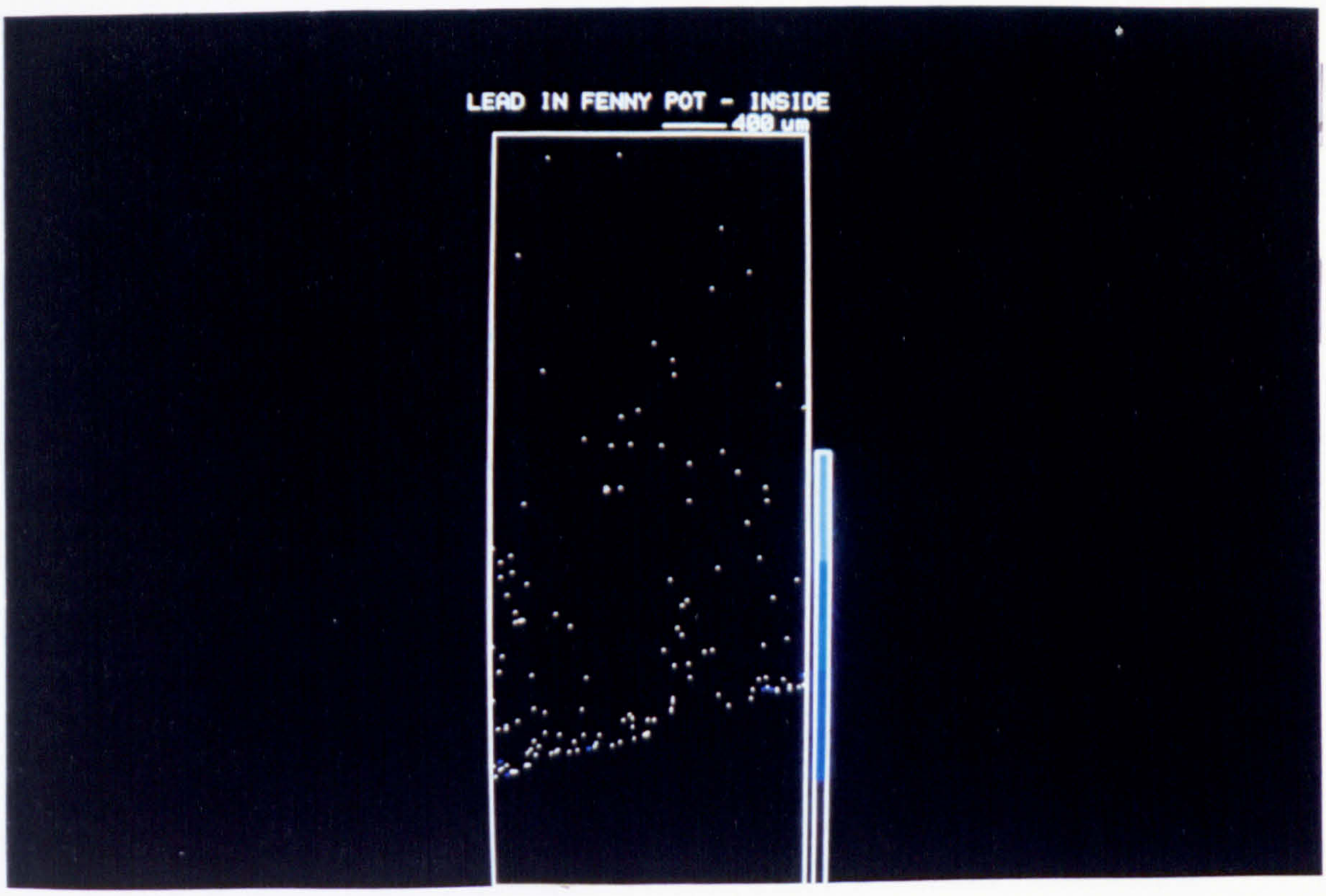
90


CAMECA Image Window 1
1000 um Pot_ Fe Ka 25 kV 30 nA

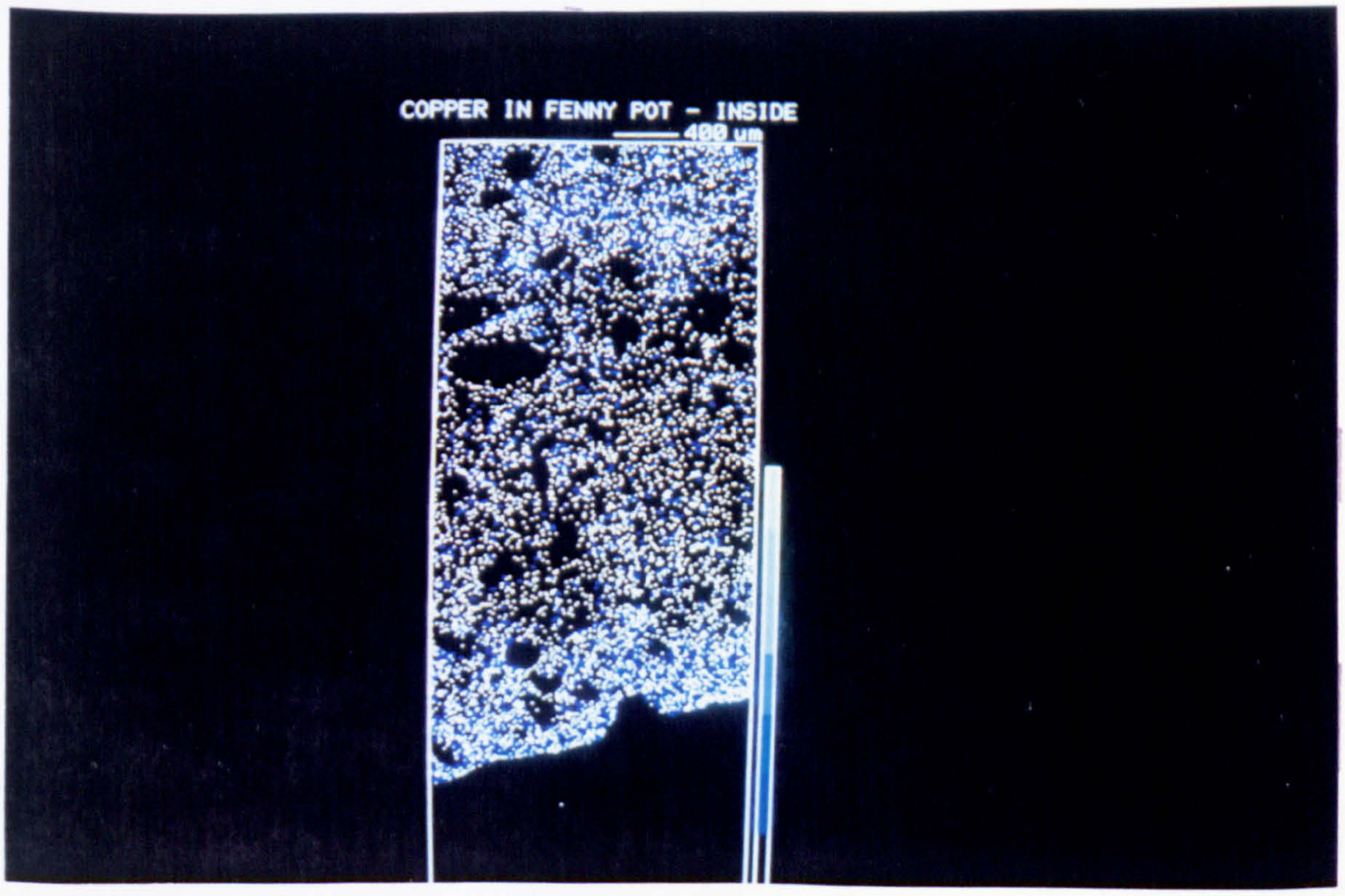
91


IRON IN FENNY POT - INSIDE
400 um

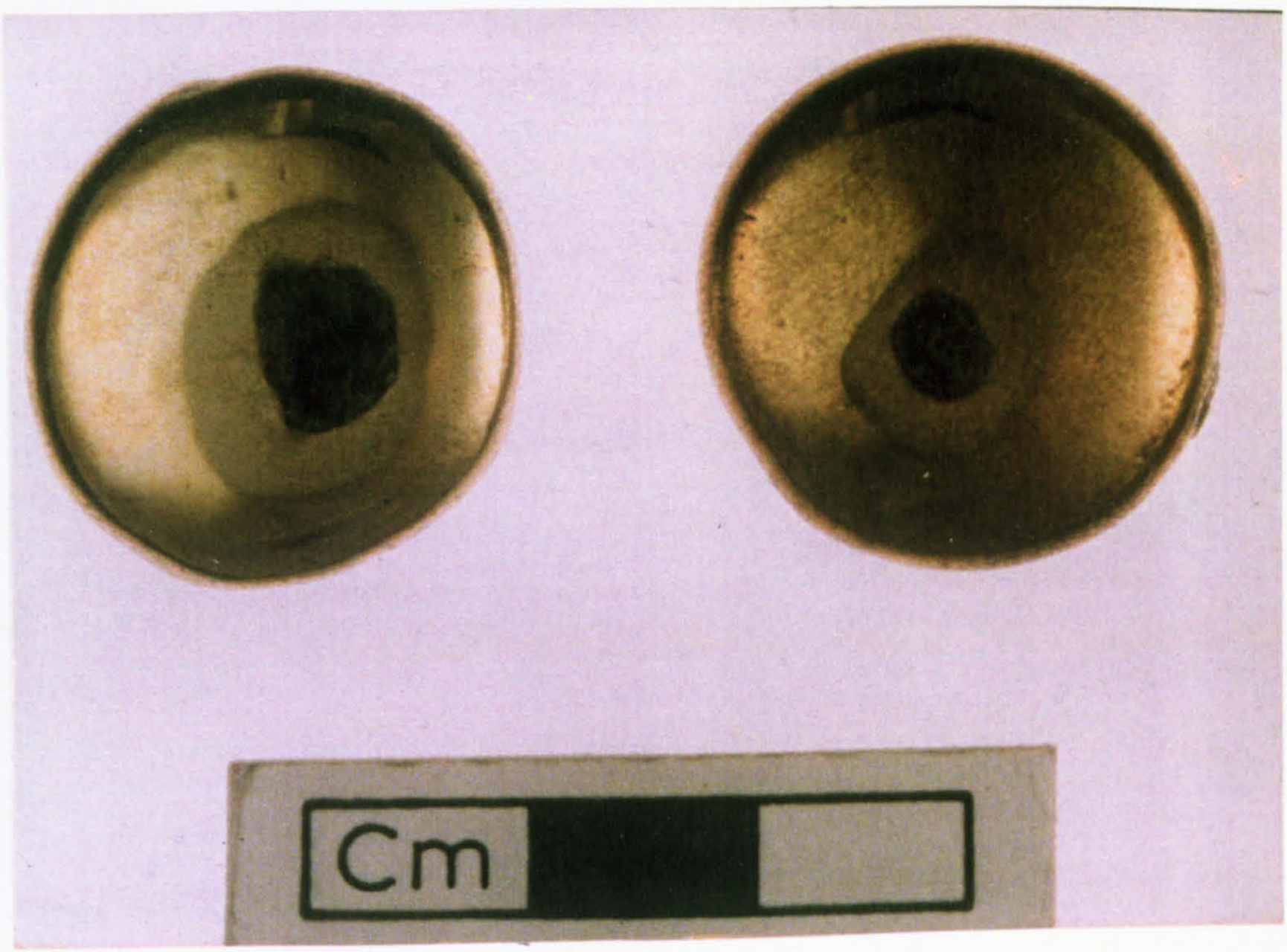
92


LEAD IN FENNY POT - INSIDE
400 um

93


COPPER IN FENNY POT - INSIDE
400 um

94



95

255